

**BULLETIN
OF THE RESEARCH COUNCIL
OF ISRAEL**

**Section A
CHEMISTRY**

Bull. Res. Counc. of Israel. A. Chem.

Page

- 1 The anion exchange of metal complexes. I. Theory
Y. Marcus and C. D. Coryell
- 17 The anion exchange of metal complexes. II. The silver-chloride
system *Y. Marcus*
- 27 The thermal hydrolysis of metal chlorides. I. Cupric chloride and
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THE ANION EXCHANGE OF METAL COMPLEXES. I. THEORY*

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Israel Atomic Energy Commission

AND

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ABSTRACT

This paper presents a comprehensive and rigorous treatment of the sorption by an anion-exchange resin of metal-anion complexes from an aqueous solution of metal M^{m+} at tracer concentration with varying concentration m_L of the ligand ion L^{l-} . This provides a functional relation between the experimental distribution coefficient D and the activity function of the ligand, $a = (L^{l-}) \gamma_{\pm}$ (ligand salt). Two assumptions regarding activity coefficients are proposed and analyzed; these make the equations much simpler and provide a set of association constants β_n^* for the complexes in solution and one parameter rK^* for binding in the ion exchanger. Further simplification may be made if one resin species, $ML_{p+m/l}$ predominates at all times in the resin phase. If the ratio m/l is an integer, an attractive alternative analysis of the sorption process and the complexing processes in the aqueous solution is made with reference to the neutral complex $ML_{m/l}^0$.

The chemical implications of the procedures and of the activity-coefficient assumptions are discussed. Two methods are presented to determine experimentally the function rF_a which corrects for change in ligand activity in the resin phase by invasion; one of these is based on direct measure of the invasion of the resin by the ligand electrolyte $C_i^{c+} L_e^{l-}$, and the other is based on study of the distribution coefficient for a stable tracer anion B^{b-} with varying concentration of ligand electrolyte. The methods are illustrated by application to the systems cadmium-sodium bromide and zinc-lithium chloride. Comparison of the solution complexity constants is made with those obtained by other workers with electro-metric methods.

* A preliminary presentation of the contents of this paper was given at the 15th meeting of the Israel Chemical Society, Haifa, April 1954; further elaboration was given at the 132nd meeting of the American Chemical Society, New York, September 1957.

** Louis Lipsky Fellow at the Weizmann Institute of Science, Rehovot, Israel, 1953-1954.

INTRODUCTION

A large body of data exists on anion-exchange equilibria of metal complexes, particularly in hydrochloric acid systems, as covered in the comprehensive review of Kraus and Nelson¹. Much of this was obtained by Kraus and co-workers².

The data are of very great importance in deriving methods of separation of different metallic elements. The data should also offer possibilities for interpreting the equilibria involved in complex formation in the aqueous phase, when suitable account has been taken of the complex species in the anion exchanger phase, the partition of complexing ligand between the two phases, and activity coefficient relations. Kraus and coworkers² presented principally qualitative conclusions in their individual studies. Kraus and Nelson gave thoughtful consideration to identification of the principal species in the aqueous phase¹, treating activity coefficient problems conservatively. We feel that even with present imperfect knowledge, more information can be obtained by analyzing anion exchange data.

Fronaesus³ laid the foundation for a general analysis in terms of stepwise formation of complexes, for an ideal case with constant activity coefficients and negligible electrolyte invasion of the resin. We have been concerned⁴⁻⁶ with removing the limitations of the ideal case, with extending the application to systems where no neutral complex is formed^{6,7}, to developing chemical substantiation^{4,6}, and to comparing the solution complexity obtained with that derived by other physico-chemical methods. The second paper in this series⁸ presents data for the system silver-chloride. Further papers by the same author in preparation cover the systems cadmium-chloride, iron (III)-chloride, and uranium (VI)-phosphate. The system silver-thiosulfate has been presented⁷.

SIMPLIFIED TREATMENT

Let us consider a metal M^{m+} forming in aqueous solution a stepwise series of mononuclear complexes ML_n^{m-n} with the univalent ligand L^- , extending up to the coordinatively saturated complex ML_N^{m-N} . In the limiting case of unimportant changes in activity coefficients, the fraction of metal f_m in the neutral complex ML_m is given by the equation:

$$f_m = (ML_m)[\sum (ML_n)]^{-1} = \beta_m (L)^m [\sum \beta_n (L)^n]^{-1} \quad (1)$$

where β_n is the Bjerrum association constant for the n^{th} complex and (L) is the concentration of free L^- . A maximum occurs for f_m when Bjerrum's average ligand number \bar{n} has the value m .

Let us now consider an anion exchange resin R^+L^- with counter ions L^- in equilibrium with an aqueous solution of the metal M^{m+} at low concentration in a solution of the strong electrolyte C^+L^- at an arbitrary concentration. The aqueous solution will contain all the ML_n^{m-n} complexes according to the $\beta_{(n)}$ values and the free L^- concentration, which equals the total L^- concentration under the present conditions. The distribution coefficient D of metal between the anion-exchanger phase

and the aqueous phase is, in the ideal case of negligible invasion of the resin phase by C^+L^- , simply proportional to f_m :

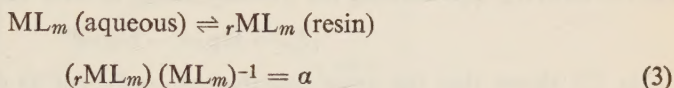
$$D = \Sigma(rML_n) / \Sigma(ML_n) = K_r f_m \quad (2)$$

or expanding f_m and putting in logarithmic form:

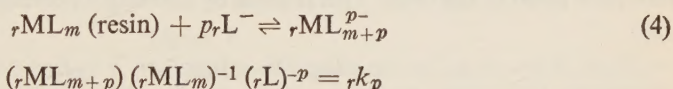
$$\log D = \log K_r + \log \beta_{(m)} + m \log (L) - \log \Sigma \beta_{(n)} (L)^n \quad (2a)$$

as shown thermodynamically by Fronaeus³, without further elaboration. In this and in later expressions presubscript r will designate terms in the resin phase.

The derivation of equation (2) may be visualized by invoking the transfer of neutral complex ML_m from the aqueous phase into the resin phase to give some rML_m , not further complexed with L^- :



followed by complex formation with an average of p ligands in the resin*:



Steps (3) and (4) do not depend in the ideal case on the variable (L) in the aqueous phase. We can make the identification of K_r in Eq. (2) as

$$K_r = \alpha \cdot r k_p \cdot (rL)^p \quad (5)$$

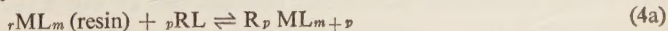
The parameter K_r represents the maximum value observed for the gross distribution coefficient D for the metal divided by the maximum value possible for f_m , a number expected to be close to unity.

Experience shows that integral values of p are found for most metal-complex-resin systems, which can be identified with $N-m$, the number of ligands to give in the resin phase the coordinatively saturated complex. It is interesting, thus, to compare $\alpha \cdot r k_p$, the equilibrium constant for transformation of aqueous ML_m to coordinatively saturated resin-held rML_N with the corresponding aqueous equilibrium constant $\beta_{(N)} \beta_{(m)}^{-1}$.

Before giving a complete treatment with all activity coefficient effects taken into account, it is convenient to outline the procedure to handle invasion of the resin by electrolyte C^+L^- , which has the effect of increasing $(rL)^p$ in Eqs. (4) and (5). Using brackets for activities, the Donnan equilibrium is represented as:

$$[C][L] = [rC][rL] = (rC) (rL) r\gamma_{\pm}^2 \quad (6)$$

* Eq. (4) could alternatively be written:



The term $\Sigma(rML_n)$ is identified as rML_{m+p}^{p-} or $R_p ML_{m+p}$.

where γ_{\pm} is the Lewis mean ionic activity coefficient of the electrolyte. We shall find it convenient to have symbols a and ${}_ra$:

$$a = (L) \gamma_{\pm} \quad \text{and} \quad {}_ra = ({}_rL) \cdot {}_r\gamma_{\pm} \quad (7)$$

Since $({}_rC)$ and $({}_rL)$ can be determined experimentally and expressed as functions of a^2 , we see from Eq. (6):

$$\log {}_ra = \log a + 1/2 \log ({}_rL) - 1/2 \log ({}_rC) \quad (8)$$

We will define a reference point for ${}_ra$, as ${}_ra^0$ at $a = 1$, a point where resin invasion is known to be small^{9,10}, but still accessible to reasonably accurate measurement. Efforts to make the reference state that of zero invasion lead to difficulties, probably partly based on impurities in the resin. We now have a logarithmic correction term ${}_rF_a$ representing the increase in $\log {}_ra$ over the reference point:

$${}_rF_a = \log {}_ra - \log {}_ra^0 \quad (9)$$

Eq. (5) shows that the gross distribution coefficient D depends on $({}_rL)$. We can correct for changes in this caused by invasion by using Eq. (9) to refer it to the same reference point in the resin. This is done by defining a corrected distribution coefficient D^0 ;

$$\log D^0 = \log D - p \cdot {}_rF_a \quad (10)$$

The distribution coefficient D^0 should be a function of complex formation in the aqueous solution only. From detailed observation of its dependence on a or the concentration (L) , the whole body of solution complex-formation constants $\beta_{(1)} \dots \beta_{(N)}$ may be determined. Figure 1 shows schematically how the functions f_m , D , ${}_rF_a$ and D^0 depend on a for a model system.

A special problem arises if the cation C^+ enters into solution complexes. When $C^+ = H^+$ this may occur at high acidities, and species H_sML_n will be formed. It is very unlikely, however, that such species form to an appreciable extent in the resin phase. The formation constant of H_sML_n is represented by $({}_s)\beta_{(n)}$; terms $({}_s)\beta_{(n)} (H)^s(L)^n$ must be included in the summation of Eqs. (1) and (2). Chemical considerations indicate that these un-ionized complex-acids will only form at $n > m$, with s of one or two. Thus these terms tend to lower f_m of Eq. (2) at high HL concentration more rapidly than would occur in the absence of participation of cations in the complexes. The equilibrium of formation of H_sML_n from $H_{s-1}ML_{n-1}$ has the simple form:

$$(H_sML_n) (H_{s-1}ML_{n-1})^{-1} = ({}_s)\beta_{(n)} \cdot {}_{s-1}\beta_{n-1}^{-1} \cdot a^2 \quad (11)$$

In an analysis of the curve $\log D^0$ vs. $\log a$, H atoms in the complex have the same consequence as L atoms. The formation of such complexes is disclosed by comparing D^0 curves for different cations, using the different ${}_rF_a$ corrections for each electrolyte, and noting systematic differences between the D^0 curve for H^+L^- and those for salt electrolytes C^+L^- .

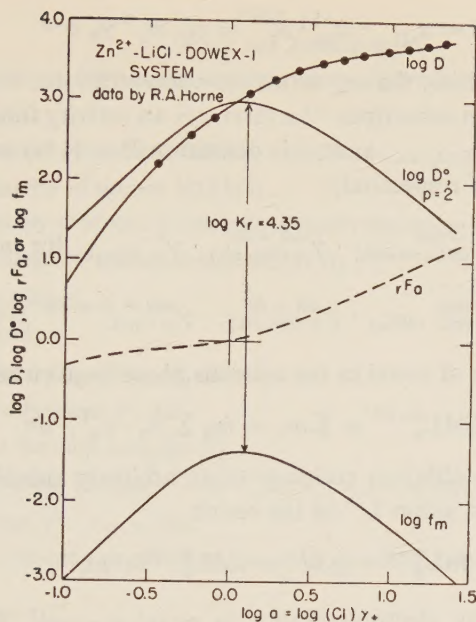


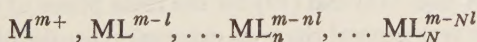
Figure 1

Model System for Zn^{2+} -LiCl-Dowex 1. The $\log f_m$ curve is based on $\log \beta_1 = 0.50$, $\log \beta_2 = -1.00$, $\log \beta_3 = 0.00$, and $\log \beta_4 = -1.00$. The rF_a curve is based on unpublished experiments of Y. Marcus and of K. A. Kraus. The observed $\log D$ data are taken from Horne²⁰. The curves interrelate by: $\log D - 2rF_a = \log D^0 = \log K_r + \log f_m$, with $\log K_r = 4.35$.

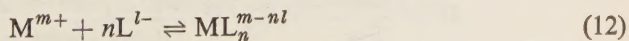
COMPLETE TREATMENT

It is of interest to see how comprehensive and how rigorous a treatment can be given to the problem of the interpretation of data for the distribution coefficient D as a function of electrolyte concentration in the anion-exchanger uptake of metal complexes. We shall start with one restriction, that the metal M^{m+} be at sufficiently low concentration, so as not to perturb the properties of the anion-exchange resin or aqueous phase, and not to participate appreciably in polynuclear complex formation.

Let L^{l-} be the ligand of arbitrary negative charge l , coming with the cation C^{c+} from the strong electrolyte $C_{l/c}L$. (See Table I for a complete list of symbols.) Now consider the complete series of complexes:



in which the particular complex ML_n^{m-nl} is formed by the equilibrium:



with the thermodynamic equilibrium constant*

* Note change from $\beta_{(n)}$ of Eq. (1), which is a concentration quotient.

$$\beta_n = a_{ML_n} \cdot a_M^{-1} \cdot a_L^{-n} = m_n m_0^{-1} \gamma_n a^{-n} \quad (13)$$

The a_x terms are activities, the m_x terms are concentrations, and electrical charges have been dropped from subscripts. The term a is an activity function defined in Eq. (7) above, namely $m_L \gamma_{\pm(C_l/cL)}$, and γ_n is defined in Eqs. (14a) and (14b) for cationic and anionic complexes respectively:

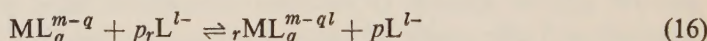
$$\gamma_n = \gamma_{\pm}^{1-n+m/l} [IML_n, (m-n)L] \cdot \gamma_{\pm}^{-(m+l)/l} (IM, mL) \cdot \gamma_{\pm}^n (C_l/cL) \text{ for } m \geq nl \quad (14a)$$

$$\gamma_n = \gamma_{\pm}^{1+(nl-m)/c} [nl-m]C, cML_n \cdot \gamma_{\pm}^{-(m+l)/l} (IM, mL) \cdot \gamma_{\pm}^{[m(l+c)-nl^2]/lc} \text{ for } m \leq nl \quad (14b)$$

The total concentration of metal in the aqueous phase is given as:

$$\sum ML_n^{m-nl} = \sum m_n = m_0 \sum \beta_n \cdot \gamma_n^{-1} \cdot a^n \quad (15)$$

Consider now the equilibrium exchange of an arbitrary anionic complex of index $q > m/l$ with the ligand anion L^{l-} in the resin:



where p is required by electroneutrality to equal $q - m/l$. The thermodynamic equilibrium constant for reaction (16) is ${}_r K_p$, related as follows to aqueous-phase and resin-phase activities:

$${}_r a ML_q = {}_r K_p \cdot a_{ML_q} \cdot {}_r a_L^p \cdot a^{-p} \quad (17)$$

and as follows to concentrations and activity coefficient terms:

$${}_r m_q = {}_r K_p \cdot \Gamma_p \cdot m_q \cdot {}_r a^p \cdot a^{-p} \quad (18)$$

where the only new term is Γ_p , a ratio of mean ionic activity coefficients in the two phases:

$$\Gamma_p = \left(\frac{\gamma_{\pm}}{{}_r \gamma_{\pm}} \right)^{1+p/lc} ({}_p l/c C, ML_q) \cdot \left(\frac{{}_r \gamma_{\pm}}{\gamma_{\pm}} \right)^{p/lc} (C_l/cL) \quad (19)$$

By expressing m_q in Eq. (18) in terms of $\sum m_n$ from Eqs. (13) and (15), we find that:

$$\frac{{}_r m_q}{\sum m_n} = \frac{{}_r K_p \cdot \Gamma_p \cdot {}_r a^p \cdot a^{m/l} \cdot \beta_q \cdot \gamma_q^{-1}}{\sum \beta_n \cdot \gamma_n^{-1} \cdot a^n} \quad (20)$$

By using the analogs of Eqs. (13) and (15) for the resin phase to express ${}_r m_q$ in terms of $\sum {}_r m_n$, we obtain the very general rigorous expression for the distribution coefficient D :

$$D = \frac{\sum {}_r m_n}{\sum m_n} = {}_r K_p \cdot \Gamma_p \frac{\beta_q \cdot {}_r \gamma_q \cdot a^{m/l}}{{}_r \beta_q \cdot \gamma_q \cdot {}_r a^{m/l}} \frac{\sum {}_r \beta_n \cdot {}_r \gamma_n^{-1} \cdot {}_r a^n}{\sum \beta_n \cdot \gamma_n^{-1} \cdot a^n} \quad (21)$$

It may be supposed that only one complex, say ${}_r ML_q^{m-q}$ will be present to an

TABLE I

Symbols and Definitions

The numbers in parentheses refer to the equations where the symbols are defined or first appear.

$a \equiv m_L l - \gamma_{\pm}(C_{i/c} L)$ (7)

a^0 value of a at reference point for which $a = 1$ (9, 28)

a'_0 thermodynamic activity of neutral ML_v^0 (36)

a_X thermodynamic activity of species X; for sake of clarity the charge on X is not stated (13)

B^{b-} stable anion of charge $b-$ (trace concentration) (31)

C^{c+} non-complexing cation

$C_{i/c}L$ supporting electrolyte

D distribution coefficient $\Sigma m_X / \Sigma m_X$ (2, 21, 40)

rF_a invasion correction function (9, 28)

f_m fraction of metal in the m -th complex (1)

i charge number (il is actual charge), $v - N < i < v$, $i = v - n$ (35)

\bar{i} average charge number, $\bar{i} = v - \bar{n}$ (44c)

K_r , rK_p , rK^* , rK , K_r constants or presumed constants involving transfer across phase boundary (2, 17, 22, 29, 41)

rK_p association constant in the resin phase (4)

L^{i-} ligand anion

M^{m+} metal forming mononuclear complex (trace concentration)

$m'_i \equiv m_{ML_{v-i}^{ii}}$ applies only for integral v (36)

$m_n \equiv m_{ML_n}^{m-ni}$ (13)

N coordination number, limiting ligand number

n number of ligands, $0 < n < N$

\bar{n} average ligand number

$p = q - m/l$, number of ligands involved in an exchange reaction (16); number of ligands in excess of m/l in the principal complex in the resin (20, 29, 41)

q arbitrary ligand number, $q > m/l$ (16)

r presubscript for ion-exchange resin phase

s number of hydrogen ions associated with complex (11)

$v \equiv ml^{-1}$

α distribution constant for neutral complex

$\beta_{(n)}$, $\beta_{(s)}$, $\beta_{(n)}$, β_n^* , β_n' , β_i' , $\beta_i'^*$, overall association constants for formation of the indicated complexes (1, 11, 13, 23, 36, 41)

Γ_p defined activity coefficient function (19)

γ_n , γ'_i defined activity coefficient functions (14, 37)

$\gamma_{\pm X}$ mean activity coefficient of component X, in supporting electrolyte $C_{i/c}L$

() parentheses for concentration of species X (1)

[] brackets for activity of species X (6)

' prime for symbols in treatment referred to neutral complex (36)

* asterisk for symbols assumed constant

appreciable extent in the resin phase. Such a supposition permits the much simpler Eq. (20) to be the expression for the distribution coefficient.

We will now explore the explicit assumptions necessary to reduce Eqs. (20) and (21) to simpler equations of the form presented in the previous section.

Assumption 1 is that Γ_p of Eq. (19) is independent of a . Both factors in Eq. (19) measure differences in mean activity coefficients on opposite sides of the phase boundary, and the inverse ratio of the ratios is taken. At very low concentrations, the mean activity coefficients will be close to unity, and the ratios will not depend much on a . At very high concentrations the two phases become very much alike, so again the ratios are close to unity. It may be noted that $p \cdot l/c$ is one or two for many metal-ligand systems.

Assumption 2 is that the ratio $\gamma_q \cdot \gamma_n^{-1}$, e.g. in Eq. (20), is essentially independent of a for successive n values in the successive regions where each ML_n^{m-n} is the prominent complex. It should be recalled that in the power series $\sum \beta_n a^n$ successive terms in general predominate in turn. Thus we can examine the ratio $\gamma_q \cdot \gamma_n^{-1}$ for successive n values, rather than the full relation presented in Eq. (20). It is also noted from the definition of γ_n in Eqs. (14a) and (14b) that the ratio $\gamma_q \cdot \gamma_n^{-1}$ always has the same total power of mean activity coefficients in both numerator and denominator. The ratio is unity at $n = q$, and by charge symmetry also at $n = m - p$. In concentrated electrolytes the charge terms become less prominent and the activity effects depend on chemical properties, thus each of the ratios should tend towards constancy, as Bjerrum¹¹ has already pointed out.

Accepting these two assumptions, let us now define the following quantities, which are thus assumed to be constants:

$$rK^* = rK_p \cdot \Gamma_p \cdot \beta_q \quad (22)$$

$$\beta_n^* = \beta_n \cdot \gamma_q \cdot \gamma_n^{-1} \quad (23)$$

The distribution coefficient D , defined by Eq. (20) will then have the logarithmic form:

$$\log D = \log rK^* + p \log ra + m/l \log a - \log \sum \beta_n^* \cdot a^n \quad (24)$$

The variable ra , which was defined as $r m_L \cdot r \gamma_{\pm(C_{i/c}L)}$, may also be defined in terms of a . Consider the equilibrium of invasion of electrolyte $C_{i/c}L$ into the resin:

$$ra_{C_{i/c}L} = a_{C_{i/c}L} \quad (25)$$

which may be expressed as:

$$r m_C^l \cdot r m_L^c \cdot r \gamma_{\pm(C_{i/c}L)}^{c+l} = m_C^l \cdot m_L^c \cdot \gamma_{\pm(C_{i/c}L)}^{c+l} = (l/c)^l a^c + l \quad (26)$$

from which it is easily derived that:

$$\log ra = \log a + l(c + l)^{-1} [\log r m_L - \log r m_C + \log(l/c)] \quad (27)$$

The value of ra is thus obtained by measuring $r m_L$ and $r m_C$ for varying values of a . Defining a reference point for the resin as ra^0 at $a = 1$ (see previous section), the function rF_a is now defined:

$$rF_a = \log ra - \log ra^0 = \log a + l(c + l)^{-1} (\log r m_L / r m_L^0 - \log r m_C / r m_C^0) \quad (28)$$

Since ${}_r a^0$ is constant for a given resin-ligand electrolyte system, a new constant ${}_r K = {}_r K^* ({}_r a^0)^p$ is defined, transforming Eq. (24) into:

$$\log D = \log {}_r K + p \cdot {}_r F_a + ml^{-1} \log a - \log \sum \beta_n^* a^n \quad (29)$$

This general equation has as its only restriction the selection of a unique value of q to describe the predominant resin species of the metal. A somewhat more complicated equation, with this restriction removed, can be derived from Eq. (21).

If the two assumptions introduced above are accepted, then D gives by Eq. (29) a known function of a (which, being the product $m_L \cdot \gamma_{\pm(Cl/cL)}$, is a measurable and known quantity), since ${}_r F_a$ is a measurable quantity. It is convenient to define a function D^0 :

$$\log D^0 = \log D - p \cdot {}_r F_a = \log {}_r K + ml^{-1} \log a - \log \sum \beta_n^* a^n \quad (30)$$

which is independent of resin effects (provided ${}_r K$ is constant, as assumed). The slope of this function is

$$d \log D^0 / d \log a = m/l - \bar{n} \quad (31)$$

where \bar{n} , the average ligand number, is $d \log \sum \beta_n^* a^n / d \log a$ in Bjerrum's nomenclature. Note first that this simple relation is true only of the slope of the corrected distribution function D^0 , and not for the observed distribution coefficient D . Note also that no restrictions whatsoever have been made on the indexes* m , l , and c . Thus Eqs. (29), (30), and (31) hold also for non-integral values of m/l .

Although not many studies of systems of fractional m/l have been reported, these still constitute important cases. The systems that have been studied, silver-thiosulfate⁷ and alkaline earth elements-citrate¹² completely bear out the predictions made from these equations. It is interesting to note that already Fronaeus³ stated that a relation of the form Eq. (31) for the slope should hold, irrespective of m/l being integral or not.

Consider the special case of the anion exchange of a stable anion B^{b-} with the ion ${}_r L^{l-}$. The behavior of this ion at tracer concentration will be covered by the preceding equations if m is replaced by $-b$ and n is set equal to zero. Note that β_0 is unity, and p now becomes $b \cdot l^{-1}$ since q is zero. Thus Eq. (29) becomes:

$$\log D \text{ (for } B^{b-}) = \log {}_r K + bl^{-1} \cdot {}_r F_a - bl^{-1} \log a \quad (31)$$

Provided that ${}_r K$ is constant as discussed above (essentially under assumption 1), the slope of the corrected distribution curve will be the simple number $-bl^{-1}$:

$$d \log D^0 / d \log a = d (\log D - bl^{-1} \cdot {}_r F_a) / d \log a = -bl^{-1} \quad (32)$$

* If we consider the system dealt with in the previous section, where $l = c = 1$, we obtain for $\log {}_r a$ Eq. (8) from Eq. (27). Remembering the definition of f_m in Eq. (1), which may be given as

$$\log f_m = \log \beta_m + m \log (L) - \log \sum \beta_n \cdot (L)^n \quad (1a)$$

and substituting in Eq. (30) for the ideal case discussed $a = (L)$, $\beta_n^* = \beta_n$, and ${}_r K = K_r \beta_m$, we obtain:

$$\log D^0 = \log K_r + \log \beta_m + m \log (L) - \log \sum \beta_n (L)^n = \log K_r + \log f_m \quad (30a)$$

Eq. (30a) is thus equivalent to Eq. (2a), while showing in its derivation what factors the latter neglects and what assumptions underlie Fronaeus' result.

This relation is important, since it gives us a means to obtain rF_n in a way less tedious than its direct measurement and calculation from Eq. (28). If the constancy of rK is accepted, then one can construct the straight line

$$\log D^0 = \log D \text{ (at } a = 1) - bl^{-1} \log a \quad (33)$$

and obtain rF_a from the difference between the observed $\log D$ for the ion B and this straight line:

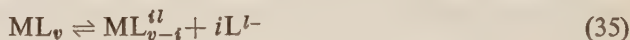
$$rF_a = lb^{-1} (\log D - \log D^0) \quad (34)$$

It should be recalled that rF_a is a property only of the resin material and the supporting electrolyte C_iL_c .

TREATMENT FOR A COMPLEX SERIES REFERRED TO NEUTRAL ML_v^0

In cases where the ratio m/l is an integer v , a neutral complex ML_v^0 exists in the series of complexes which extends from charge $m+$ to negative charge $m-Nl$. For such systems, a much more elegant derivation of equations describing the variation of D with a may be made, as pointed out to us by Professor Scatchard (Massachusetts Institute of Technology). There is no great advantage in extending this treatment to non-integral values of m/l . Cases of a series with a neutral complex (especially for $l = 1$) constitute the majority of the systems studied to date.

Let us define the formation of a complex by relating it to the neutral complex ML_v :



where the index i may be called the "charge number" of the complex ML_{v-i}^{ii} , giving its charge in terms of the ligand charge $l-$. The charge number can take the values $v - N \leq i \leq v$, and obviously can be related to the index n used in the previous section by $i = v - n$. An average charge number \bar{i} can be defined analogously to the average ligand number \bar{n} by $\bar{i} = v - \bar{n}$.

Consider now the thermodynamic equilibrium constant for reaction (35):

$$\beta'_i = a_{ML_{v-i}} a_L^i a_{ML_v}^{-1} = m'_i \gamma'_i a^i a_0'^{-1} \quad (36)$$

where m'_i is the concentration of the i -th complex species, a is the ligand activity function $m_L \cdot \gamma_{\pm(C_i/L)}$ used before, a'_0 is the thermodynamic activity of the neutral complex ML_v , and γ'_i is given by

$$\gamma'_i = \gamma_{\pm(ML_{v-i}, iL)}^{1+i} \cdot \gamma_{\pm(C_i/L)} \quad \text{for } i > 0 \quad (37a)$$

$$\gamma'_i = \gamma_{\pm(i/l C, ML_{v-i})}^{1-ill/c} \cdot \gamma_{\pm(C_i/L)}^{ill/c} \quad \text{for } i < 0 \quad (37b)$$

Primes are used to distinguish the conventions of this treatment from those of the preceding section. The total aqueous metal concentration is then given by

$$\Sigma m'_i = a'_0 \Sigma \beta'_i \gamma'^{-1}_i a^{-i} \quad (38)$$

A corresponding equation holds for the series of complexes m_i in the resin. At equilibrium the simple relationship

$$ra'_0 = a'_0 \quad (39)$$

holds and thus the distribution coefficient is given by

$$D = \Sigma m'_i / \Sigma m_i = \Sigma r\beta'_i \gamma'^{-1}_i a^{-i} / \Sigma \beta_i \gamma_i^{-1} a^{-i} \quad (40)$$

Let us for the sake of simplicity again introduce the restriction of considering $\Sigma r m'_i = r m_{-p}$ where $-p$ is the charge number of the principal species present in the resin phase. Let us furthermore introduce assumptions analogous to those considered in the previous section:

Assumption 1' is that $r\gamma'_{-p}$ is independent of a .

Assumption 2' is that successive γ'_i values are essentially independent of a in the successive regions where the corresponding species ML_{v-i} are predominant.

We now define the quantities $K'_r = r\beta'_{-p} \cdot r\gamma'^{-1}_{-p} \cdot (ra^{0p})$ and $\beta_i'^* = \beta_i \cdot \gamma_i'^{-1}$, which are constants if the above assumptions are accepted, and have for the distribution coefficient

$$\log D = \log K'_r + p r F a - \log \Sigma \beta_i'^* a^{-i} \quad (41)$$

and for the corrected distribution coefficient

$$\log D^0 = \log D - p r F a = \log K'_r - \log \Sigma \beta_i'^* a^{-i} \quad (42)$$

Finally, for the slope of the corrected distribution coefficient we have

$$d \log D^0 / d \log a = - d \log \Sigma \beta_i'^* a^{-i} / d \log a = \bar{i} \quad (43)$$

The two methods of formulating anion exchange equilibria of a metal-ligand system are fully equivalent. Eqs. (21) and (40) are the most general formulations. The pairs of assumptions leading to either Eq. (29) or Eq. (41) are equivalent. If these assumptions are not valid, Eqs. (29) and (41) can be treated as general, but the presumed constants rK and β^* (or their primed analogs) will be functions of a . The assumption that the complex in the resin phase can be represented as the anion ML_q^{m-q} (or ML_{v+p}^{pl}) is purely a convenience, but one that corresponds rather well to the general behaviour of metal complexes in anion-exchange resins.

Equations (41), (42), and (43) are alternative to Eqs. (29), (30), and (31), with the three identifications:

$$K'_r = rK \cdot \beta_v^{*-1} = K_r \quad (44a)$$

$$\beta_i'^* = \beta_n^* \cdot \beta_v^{*-1} \quad (44b)$$

$$\bar{i} = \nu - \bar{n} \quad (44c)$$

in cases where ν is an integer and therefore β_ν has direct meaning.

The treatment of a series of complexes in terms of formations of the complexes from the neutral member has very obvious advantages in any system involving transfer of material across a phase boundary, as here in anion-exchange equilibria, or in solvent extraction equilibria, as pointed out by Poskanzer¹³. Such a treatment leads to the terms i for charge number and \bar{i} for average charge number, both expressing the charge in units of l , the ligand charge. These terms have rather general usefulness.

CHEMICAL SUBSTANTIATION

It is of interest to see how effectively the equations of either of the previous two sections provide a mechanism for expressing in detail observed physicochemical behaviour of metal-ligand systems. If the β_n values are known for the solution equilibria among the complexes, the whole ion-exchange distribution can be predicted from a measurement of D at one a value (to determine ${}_rK$), provided the ${}_rF_a$ function has been determined and p can be assumed. If p is not known, another measurement of D at a point of considerably different ${}_rF_a$ value serves to establish p . It would seem reasonable to determine p from the accepted N for the metal and ligand, thus $p = N - m/l$. If ${}_rF_a$ is sensibly constant, p is not a required parameter.

Conversely, if an extended body of data for D vs a is available, along with ${}_rF_a$, standard methods of analysis can be used to obtain the parameters (constants) ${}_rK$ and the set of β_n^* values. These can be compared with corresponding $\beta_{(n)}$ values or thermodynamical β_n values from potentiometry, polarography, spectrophotometry, and other methods, with due regard for differences in treatment of activity coefficients. Although the ionic strength is variable in this type of study, the successive β_n^* values may be considered valid for successive regions of constant ionic strength. The approximations required to handle activity coefficient corrections are easiest to make for complexes of low charge (in the neighbourhood of $n = m/l$ or $i = 0$). The anion-exchange treatment gives best precision for the determination of constants just in this neighbourhood, whereas potentiometric methods give precision falling from best at $n = 1$. The relations among the successive β values for different metals present an interesting problem in structural inorganic chemistry.

The parameters ${}_rK$ for a given metal and ligand and ${}_rF_a$ for a given supporting electrolyte are functions of the detailed properties of the anion-exchange resin, namely chemical nature of fixed charges, capacity, and cross-linking. Practically nothing has been done to exploit these parameters as tools for the characterization of anion-exchange resins. It is also a challenge to theoretical chemistry to explain the great range of $\log {}_rK$ values that different metals show with a given ligand and a given anion-exchanger. The range goes from < 0 to > 7 .

The *cadmium-sodium-bromide* system with the anion-exchanger Amberlite IR-400 will be treated numerically, using data of Fronaeus³ presented in Table II, with the logarithm of the ligand activity function $a = (Br^-)\gamma_{\pm(Na, Br)}$ in the first column and $\log D$ in the second. Fronaeus³ was satisfied to present these data to show that D clearly goes through a maximum, as required by Eq. (2).

TABLE II
Anion-exchange data⁽³⁾ for system $Cd^{2+} - Na^+ Br^-$ - Amberlite IR-400

Logarithm of ligand activity function $\log a = \log m_{Br}\gamma_{\pm(Na^+Br^-)}$ (m_{Br} in moles/liter)	Logarithm of observed distribution coefficient $\log D$ (liters/kg of dry resin)
-2.38	2.20
-1.43	4.30
-0.95	4.80
-0.40	4.90
-0.18	4.30
+0.17	3.65

The system belongs to the class $m = 2, l = 1, c = 1$, and it is a reasonable assumption that $N = 4$. Data are not yet available for rF_a for Na^+Br^- in Amberlite IR-400. From invasion data reported by Gottlieb and Gregor¹⁴ for K^+I^- and K^+Cl^- with a similar resin, it is probable that rF_a does not vary much over the region of concern, and it will be taken here as zero. Since rF_a does not change appreciably, we do not need a value for p . The data for $\log D$ in Table II were taken therefore as data for $\log D^0$ in Eq. (42). They were analyzed for the parameters rK' and the four β'_i values with index $i = +2, +1, -1$ and -2 by curve-fitting methods of Sillén¹⁵. The value of $\log K'_r$ was found to be 5.5. From this and the maximum $\log D$ value (4.9), it is computed that f_m , the fraction of metal in the neutral complex, has a maximum value of 0.25 at $\log a = -0.75$. The value of β_0^* is unity. The other β parameters are given in Table III, where they are compared with similar values reported from potentiometry and polarography by four other workers. The fit of the parameters to the data is shown by the smooth line in Figure 2.

The β parameters for $i = +1$ and $i = -1$ are expected to be most reliable from the anion-exchange analysis, particularly as the fraction of $CdBr_2$ is at a maximum right in the middle of the set of experimental points. The agreement between our parameters and those of the other authors in Table III is satisfactory for $i = +1, -1$, and -2 . Our value of $\log \beta_{+2}^*$ is the highest in the table. It depends principally on the first experimental point. It is possible that an appreciable negative rF_a occurs below $\log a = -2$ for $NaBr$, as occurs for $LiCl$ and HCl (See Figure 1), which

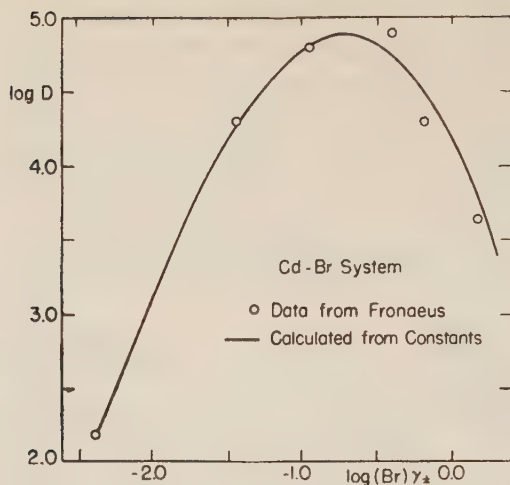


Figure 2

Fit of Fronaeus³ data by the complexity parameters for CdBr_{2-i}^i complexes: $\log \beta'_i^*$ values of $-1.7, -0.7, 0, +0.3$, and $+1.0$ for i values $+2, +1, 0, -1$, and -2 , $\log K'_r = 5.5$. Corresponding standard Bjerrum $\log \beta_{(n)}$ values for CdBr_n^{2-n} are $1.0, 1.7, 2.0$, and 2.7 for n values of 1 through 4 .

should be corrected for to give a lower $\log \beta'_{+2}^*$, perhaps near the average* of the other four values in Table III.

The zinc-chloride system with the anion-exchange resin Dowex-1 has been studied rather widely, and results up to 1955 have been summarized by Kraus and Nelson¹. New data for $\log D$ for the supporting electrolyte Li^+Cl^- have been reported by Horne²⁰, which through the courtesy of the authors are given in Figure 1 (solid circles). Also on this figure is the rF_a curve for Li^+Cl^- with Dowex-1 as a broken curve, based on unpublished experiments** of one of us and data communicated privately by Dr. Kraus. Taking direct experimental evidence²⁰ from higher loading that $p = 2$, and assuming no difference for lower loading, the experimental $\log D$ curve is transformed to the curve on Figure 1 labelled $\log D^0, p = 2$. This has been analyzed¹⁵ to give the constants $\log \beta'_i^*$ given in the following equation based on Eq. (41), covering $\log D$ over the range of $\log a$ from -1.0 to $+1.5$:

$$\log D = 4.35 + 2rF_a - \log \sum (10^{1.0} a^{-2} + 10^{0.5} a^{-1} + 1 + 10^{1.0} a + 10^{0.0} a^2) \quad (45)$$

* Assuming this corrected value, we may take our successive Bjerrum constants to be $\log \beta_1 = 1.6$, $\log \beta_2 = 2.3$, $\log \beta_3 = 2.6$, and $\log \beta_4 = 3.3$. The following ratios of these are considered quite reliable: $\log \beta_2 \beta_1^{-1} = 0.7$, $\log \beta_3 \beta_2^{-1} = 0.3$, and $\log \beta_4 \beta_3^{-1} = 0.7$.

** To be presented in a later paper of the series.

TABLE III

Comparison of formation constants for cadmium-bromide complexes

Complex formed from CdBr_2 :			Cd^{2+}	CdBr^+	CdBr_3^-	CdBr_4^{2-}
Parameter			$\log \beta'_{+2}$	$\log \beta'_{+1}$	$\log \beta'_{-1}$	$\log \beta'_{-2}$
Bjerrum equivalent:			$\log \beta_0 \beta_2^{-1}$	$\log \beta_1 \beta_2^{-1}$	$\log \beta_3 \beta_2^{-1}$	$\log \beta_4 \beta_2^{-1}$
Author	Method	Ionic Medium	Formation constant			
LEDEN ¹⁶	Potent.	3 M NaClO_4	-2.35	-0.59	0.98	1.36
ERIKSSON ¹⁷	Polarogr.	3 M NaClO_4	-2.43	-0.67	0.76	1.29
RILEY ¹⁸	Potent.	variable	-3.10	-0.92	0.30	0.90
STROCCHI ¹⁹	Polarogr.	2 M KNO_3	-2.01	-0.56	0.15	0.71
Present work		variable NaBr	-1.7	-0.7	0.3	1.0

The fit to the Horne data is excellent. The successive Bjerrum $\log \beta_n^*$ values are -0.5, -1.0, 0.0, and -1.0. The corresponding first three $\log \beta_{(n)}$ values reported by Sillén and Liljeqvist²¹ from potentiometry in 3 M NaClO_4 medium are -0.2, -0.6, and +0.15, showing the same trend, with $\log \beta_3$ the highest, but they are higher by 0.3, which may reflect a difference in activity coefficients.

The system *zinc-chloride* in the presence of hydrogen ion shows^{1,20} a curve of $\log D$ vs $\log a$ that has a maximum at $\log a = 0.3$, beyond which it falls well below $\log D$ for corresponding Li^+Cl^- concentrations. The effect can be shown not to be due to differences in rF_a , but rather that the system exhibits association of H^+ with the complex to form some hydrogen chlorozincates, such as HZnCl_4^- . The system can be treated by Eq. (11), with a new parameter for each hydrogen atom in the complex, as will be treated in a later paper of the series.

The system *silver-thiosulfate*⁷ shows the interesting properties of non-integral m/l relation. Although N is 3, p was found to be $1/2$, making the principal species in the resin AgS_2O_3^- . The value $\log \beta_3^* \beta_2^{*-1}$ was found to be +1.7. The corresponding value estimated for ionic strength 1 to 2, $\log \beta_{(3)}\beta_{(2)}^{-1}$, was +0.4.

The data for *silver-chloride* occur in the next paper⁸.

The problem of ligand hydrolysis is discussed in connection with the *uranium VI-phosphate* system in a later paper²². Side reactions such as metal hydrolysis can be handled by obvious extensions of Eqs. (21), (29), or (41).

ACKNOWLEDGEMENTS

The authors are grateful to Professor George Scatchard of the Massachusetts Institute of Technology for numerous discussions and valuable suggestions, to Dr. K. A. Kraus of the Oak Ridge National Laboratory for friendly criticism and access to unpublished data, and to Dr. Israel Dostrovsky of the Weizmann Institute of Science

for guidance. Professor Ernst D. Bergmann of the Israel Atomic Energy Commission and Mr. Meyer Weisgal and Dr. Benjamin Bloch of the Weizmann Institute of Science gave generous support to this work. The U. S. Atomic Energy Commission made it possible for the authors to complete the revision of the work at the Massachusetts Institute of Technology.

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THE ANION EXCHANGE OF METAL COMPLEXES.

II. THE SILVER-CHLORIDE SYSTEM*

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ABSTRACT

The methods developed in the first paper of this series¹ were applied to a study of the silver-chloride complex-system. The mononuclearity of the complexes was first tested and confirmed. The distribution of the silver between the resin and the solution was then measured by the aid of Ag^{110} tracer in the range 0.002–12 M hydrochloric acid. The activity function of chloride in the resin was calculated from published data, and a "corrected" distribution curve was constructed. The successive complexity constants were calculated by curve-fitting. The range of concentrations studied did not allow evaluation of β_1 for formation of the undissociated complex AgCl , but the following successive stepwise constants were found: $\log \beta_2^* \beta_1^{*-1} = 2.5 \pm 0.2$, $\log \beta_3^* \beta_2^{*-1} = 0.85 \pm 0.05$ and $\log \beta_4^* \beta_3^{*-1} = -1.0 \pm 0.2$ for the complexes AgCl_2^- , AgCl_3^{2-} and AgCl_4^{3-} respectively. These constants are compatible with published values.

INTRODUCTION

The silver-chloride system was selected for study and interpretation¹ by the anion-exchange method for a number of reasons. First, as both the silver and the chloride ions are univalent, this system is the simplest possible. Then the resin activity-function data for the ligand, needed for the calculations, are available for chloride²-hydrochloric acid. Further, the complex-formation constants of the silver-chloride system are known (see Table III), and can be used as a check on the values obtained by the anion-exchange method. On the other hand, no investigation on the anion exchange of silver from hydrochloric acid had been published before this study was begun**. Finally, the availability of the radioactive tracer Ag^{110} made the distribution measure-

* This work is taken from part of a Ph. D. thesis submitted to The Hebrew University of Jerusalem, Israel, June 1955.

** After completion of this work, K. A. Kraus and F. Nelson published a very rough representation of an anion-exchange distribution curve for silver chloride (International Conference for the Peaceful Use of Atomic Energy, Geneva, August 1955, Paper P/837.) Their results are in qualitative agreement with ours, but could not be used for quantitative comparison. These authors also stated that the distribution with lithium-chloride solutions does not differ much from that with hydrochloric acid solutions, and thus there is practically no "lithium chloride effect." The meaning of this fact will be explained in a later paper in this series.

ments very simple. One drawback for this system is the rather high stability of the complexes, so that a very wide range of ligand activities, especially at very low concentrations, had to be covered. As will appear later, even in 0.002 M solutions, the formation of the complex AgCl is already complete, so that the constant of its formation from the free Ag^+ and Cl^- ions could not be evaluated. The low solubility of AgCl is no serious difficulty, as the radioactive tracer technique made it possible to work at such concentrations that its solubility was not exceeded.

EXPERIMENTAL

Highly active silver (containing 270-day Ag^{110}) was dissolved in nitric acid, and silver chloride was precipitated by hydrochloric acid. The precipitate was washed in the dark with dilute hydrochloric acid, and then dissolved in concentrated hydrochloric acid. The solution was quite stable in daylight and did not lose its activity by reduction, precipitation on the walls of the container, or other effects. The specific activity of the silver was about 10^{10} cpm per mole. To another portion of the nitric acid solution, inactive silver nitrate was added to reduce the specific activity to 2×10^7 cpm per mole, and a similar chloride solution was prepared as before.

Solutions were prepared by mixing the silver-containing solution with varying amounts of hydrochloric acid and diluting to volume, in a volumetric flask, with distilled water. The concentration of hydrogen ions was found by titration of an aliquot with sodium hydroxide. The same amount of base was added to another aliquot, which was then titrated with silver nitrate by Mohr's method. The values obtained for H^+ and Cl^- agreed well, giving the hydrochloric acid concentration.

The resin employed was Dowex-1, 10% crosslinked, mesh size between 100 and 200. It was in chloride form, air dried, and had a capacity of 2.3 meq/g. It is similar in all respects to that used by Kraus and Moore² in their study of activity coefficients.

Aliquots of the solutions were shaken with portions of the resin, the relative amounts being 96 ± 2 ml/g. Shaking was continued for 20–24 hours (proved enough for attainment of equilibrium) at $30 \pm 2^\circ\text{C}$. The solution was separated from the resin by means of sintered glass funnels, and it was shown that no losses of silver (by absorption) occurred with this procedure.

The distribution coefficient D was calculated from the difference in silver concentration (measured by a dipping Geiger counter as cpm per constant volume) before and after the equilibration. The changes of other constituents of the solution were negligible, so that no error arose due to differences of absorption of the beta and gamma rays before and after equilibration.

Owing to the very high distribution coefficients found in some cases, the solutions were very much depleted in silver, and relatively large errors were encountered in the counting. In a similar way, in cases where the distribution was low, the amount sorbed on the resin was small, and as it was found by difference, again large errors occurred. In the range of distribution coefficients 30–3000 the statistical error of counting caused errors of about $\pm 3\%$. Beyond this range errors were larger. The

errors in ligand concentration (± 0.001 M) were negligible except in the very lowest concentrations. The measurement of liquid volumes was within $\pm 0.5\%$, that of the weights of resin within $\pm 1\%$. The minimal overall error was thus $\pm 5\%$.

RESULTS

The effect of the concentration of the silver ions on the distribution was measured, in the range 1.5×10^{-6} M to 4.6×10^{-3} M, for a number of hydrochloric acid concentrations. The values of the silver concentrations were chosen in such a way as to give maximum accuracy (50% distribution), so that for every hydrochloric acid concentration the range of silver concentrations was more limited than that appearing above. Table I gives the results of $\log D$ as a function of silver and chloride concentrations, where D is the distribution coefficient, in litres kg^{-1} , defined as total concentration of silver in the resin divided by total concentration of silver in the solution at equilibrium. The ligand activity function¹ is taken as $a = m_{\text{HCl}}\gamma_{\pm}(\text{HCl})$ with γ_{\pm} , the mean ion activity coefficient of hydrochloric acid (molar scale), taken from Harned and Owen³. The symbols have been defined in the preceding paper¹.

TABLE I
Effect of the silver ion concentration on the anion exchange distribution

Concentration of ligand m_{HCl} (moles/litre)	Logarithm of ligand activity function $\log a$	Logarithm of observed distribution coefficients for various initial total silver concentrations C_M $\log D$ (litres/kg of dry resin)*				
		5.82	5.41	-log C_M		
				4.66	4.34	2.34
0.016	-1.87	2.25	2.32			
0.030	-1.60	2.86	2.95			
0.055	-1.40	3.06			3.15	
0.110	-1.10		3.60	3.61		
0.125	-1.00		3.80		3.77	
0.46	-0.50			3.12	3.09	
0.90	-0.20			2.49	2.48	
2.8	0.60			1.50	1.52	
4.8	1.10				1.34	1.38
6.2	1.45				1.30	1.04
10.5	2.50				0.5	0.6

* The error of values in bold is larger than ± 0.05 log units, for the rest it is smaller.

The observed independence of D of the metal concentration shown in Table I gives strong indication that the complexes are mononuclear.

The effect of varying the ligand concentration was measured in the concentration range 0.002 to 12 M HCl. Results appear in Table II and in Figure 1.

TABLE II
Effect of the hydrochloric acid concentration on the anion exchange distribution

Concentration of ligand m_{HCl} (moles/litre)	Logarithm of ligand activity function $\log a$	Logarithm of distribution coefficient $\log D$ (litres/kg)*	Concentration of ligand m_{HCl} (moles/litre)	Logarithm of ligand activity function $\log a$	Logarithm of distribution coefficient $\log D$ (litres/kg)*
0.002	-2.8	1.61	0.31	-0.60	3.12
0.003	-2.5	2.09	0.46	-0.50	3.07
0.006	-2.24	2.17	0.62	-0.35	2.81
0.008	-2.13	2.36	0.77	-0.28	2.61
0.011	-2.00	2.40	0.90	-0.20	2.48
0.016	-1.87	2.70	1.80	0.25	1.92
0.031	-1.58	2.95	2.8	0.60	1.52
0.060	-1.33	3.26	4.8	1.10	1.38
0.077	-1.20	3.38	6.2	1.45	1.04
0.110	-1.08	3.70	7.7	1.90	0.7
0.124	-1.02	3.80	9.0	2.18	0.5
0.160	-0.94	3.38	10.5	2.50	0.6
0.200	-0.85	3.35	12.0	2.82	0.3

* The error of values in bold is larger than ± 0.05 log units, for the rest it is smaller.

DISCUSSION

Figure 1 shows a curve of $\log D$ vs. $\log a$, the chloride activity function, consisting of an ascending branch (up to 0.12 M HCl) and a descending one. The latter is concave upwards; this would mean a decrease of the ligand number function \bar{n} (which is unreasonable), were it not for changes of the activity of the ligand in the resin. This factor makes it necessary to calculate a D^0 curve by Eq. (30) of reference (1) (Part I), giving by its slope the true average ligand number \bar{n} , according to Eq. (31) of Part I.

The correction function rF_a is given by Eqs. (8) and (9) of Part I. Values for hydrochloric acid-Dowex-1 resin can be calculated from activity coefficient data of Kraus and Moore². It is assumed that the Dowex-1 resin sample employed in the present investigation has the same invasion characteristics of the sample used by the above authors. From their data, a value $\log r\alpha^0 = 0.46$ was calculated, and the correction function is then obtained from:

$$rF_a = \log r m_{\text{Cl}} + \log r \gamma_{\pm(\text{HCl})} - 0.46 \quad (1)$$

A plot of rF_a vs. $\log a$ is shown in Figure 2. The corrected distribution curve D^0 will be given by Eq. (30) of Part I, i.e.,

$$\log D^0 = \log D - p rF_a \quad (2)$$

The predominant resin complex could be any one of RAgCl_2 , R_2AgCl_3 and R_3AgCl_4 . Now when p is assumed to be unity, (RAgCl_2), the D^0 curve is still concave upwards.

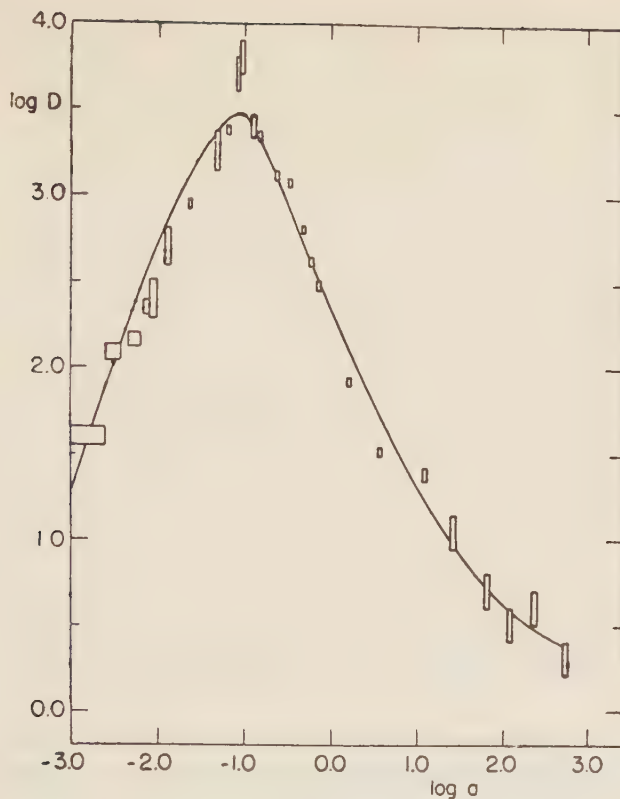


Figure 1

The anion exchange distribution curve ($\log D$) plotted against the logarithm of the chloride activity function ($\log a = \log m_{\text{HCl}} + \log \gamma_{\pm \text{HCl}}$) for the absorption of silver from hydrochloric acid by Dowex-1-chloride-anion-exchange resin. The dimensions of the rectangles indicate the probable error of the data

When p is equal to 3 the slope of the D^0 curve goes to -4 at the limit, signifying a solution complex AgCl_5^{4-} , which is improbable (unconventional coordination number). When p is equal to 2, the curve is convex upwards and the limiting slope becomes -3 , meaning that the highest complex is AgCl_4^{3-} . This is, at least, very probable. In an infrared investigation of the similar system silver-cyanide by Jones and Penneman⁴ it was shown that the principal resin species may be $\text{R}_2\text{Ag}(\text{CN})_3$, rather than the coordinatively saturated complex $\text{R}_3\text{Ag}(\text{CN})_4$. Similarly, in the system silver-thiosulfate, it was shown⁵ that the most probable resin species is RAgS_2O_3 , rather than $\text{R}_5\text{Ag}(\text{S}_2\text{O}_3)_3$. It may thus be a property of silver to form unsaturated complexes in the resin. Furthermore, work on solvent extraction with a higher amine in an organic solvent⁶ showed a second power dependence on the amine concentration, which means that R_2AgCl_3 is the main species extracted.

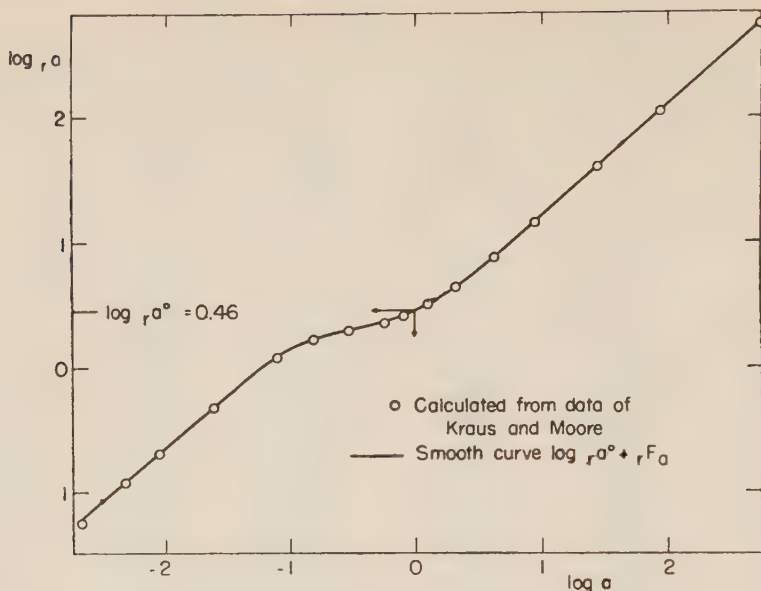


Figure 2

The activity function $r a$ of chloride in the resin Dowex-1-chloride equilibrated with hydrochloric acid plotted against the chloride activity function a in hydrochloric acid solution (logarithmic scales)

The D^0 curve was, therefore, calculated with $p = 2$, and is plotted in Figure 3. The silver-chloride complex system has a neutral member, and the curve may thus be analyzed in terms of the charge number i , which in this case equals the actual charge of the complex, the ligand charge being unity. Eqs. (42) and (43) of Part I were applied to the data, the value of the average charge number \bar{i} being found to vary from -0.4 to -2.6 , corresponding to the successive complexes AgCl , AgCl_2^- , AgCl_3^{2-} and AgCl_4^{3-} . Preliminary values of the successive formation constants β_i^*/β_{i+1}^* were first obtained by Bjerrum's method of half-integral \bar{i} (or \bar{n}) values, where to a first approximation:

$$\log \beta_i^*/\beta_{i+1}^* = -\log a_{(\bar{i} = i - 1/2)} \quad (3)$$

Since β_o^* is unity and $\beta_{+1}^* a^{-1}$ may be neglected, preliminary values of β_i^* are thus obtained, from which a correction term $\beta_{-3}^* a^3$ for the extreme complex AgCl_4^{3-} was calculated. The correction term was subtracted from K_r'/D^0 which, as obtained from Eq. (42), Part I, is:

$$K_r'/D^0 = \sum \beta_i^* a^{-i} = 1 + \beta_{-1}^* a + \beta_{-2}^* a^2 + \beta_{-3}^* a^3 \quad (4)$$

to give an equation in the three parameters K_r' , β_{-1}^* and β_{-2}^* , which could be solved by Sillen's⁷ curve-fitting method.

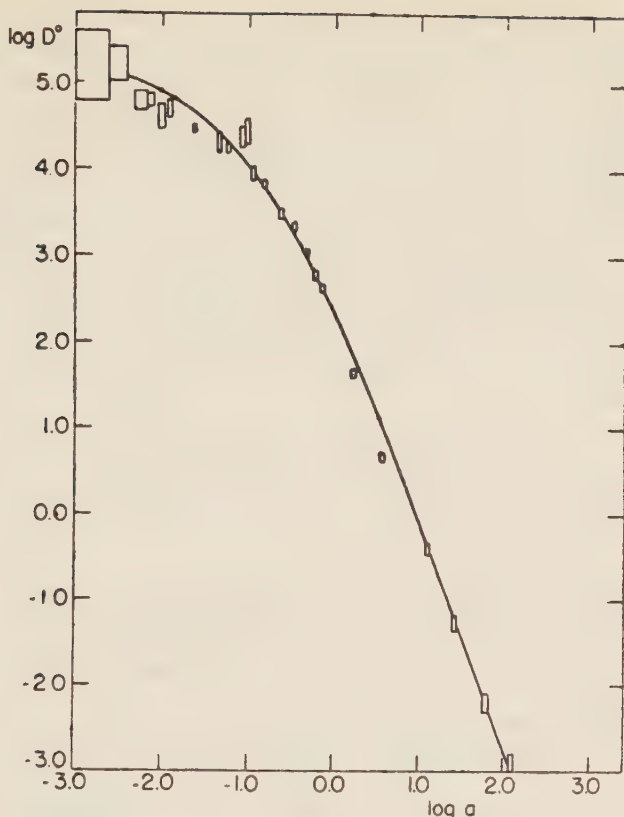


Figure 3

The corrected distribution curve ($\log D^0$), using the parameter $p = 2$ for the predominant resin species R_2AgCl_3 , plotted against the chloride activity function ($\log a$)

The value of $\beta_{-1}^{\prime*}$ was then used to obtain the values of;

$$(K_r'/D^0 - 1) (\beta_{-1}^{\prime*} a)^{-1} = 1 + \beta_{-2}^{\prime*} \beta_{-1}^{\prime*-1} a + \beta_{-3}^{\prime*} \beta_{-1}^{\prime*-1} a^2 \quad (5)$$

which could in a similar way be solved for $\beta_{-2}^{\prime*}$ and $\beta_{-3}^{\prime*}$. By such an iterative method the following final values were obtained:

$$\log K_r' = 5.70 \pm 0.05, \log \beta_{-1}^{\prime*} = 2.5 \pm 0.2, \log \beta_{-2}^{\prime*} = 3.35 \pm 0.05, \log \beta_{-3}^{\prime*} = 2.25 \pm 0.2.$$

These values were introduced into equations (41) and (42) of Part I, and the solid curves of Figures 1 and 3 were calculated, showing a good fit with the experimental data.

That the experimental data can be fitted by a power series with a limited number of parameters does not mean that these parameters are equilibrium constants. It

should be recalled (Part I) that they are products of true thermodynamic equilibrium constants and activity coefficient functions. These latter are assumed constant for the region where a definite power dependence on a , the ligand activity function, is predominant. The ability of the parameters to describe the data is an indication that this assumption is valid, or that the errors introduced by it cancel each other out.

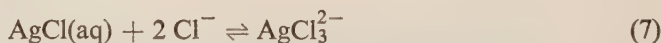
From the value of K'_r and the arbitrarily defined $\log r a^0$ the constant for the formation of R_2AgCl_3 in the resin from $AgCl$ in the solution can be derived. This "constant" has no absolute significance, being dependent on the reference state defined for the particular resin used, but it serves for comparison with the formation of other complexes in the same resin. From Eqs. (3), (4), (5) and (44a) of Part I it is seen that K'_r is the equilibrium constant (bearing the assumption concerning activity coefficients in mind) for the reaction:



times the second power of the reference state $r a^0$. The constant for equation (6) is thus readily obtained:

$$\log K_{(6)} = \log K'_r - 2 \log r a^0 = 5.70 - 2 \times 0.46 = 4.78$$

This value may be compared with the comparable value for the corresponding reaction in solution:



$\log \beta'_2 = 3.35$. It is seen that the resin stabilizes the silver complex about 30-fold.

The association constants found can be compared with those reported in the literature provided due cognizance is taken of differences in the activity coefficient functions involved*. The reported constants were recalculated to give values of $\log \beta'_i$, evaluated for constant ionic strength, when applicable, or similar "constants" for varying ionic strength, and are shown in Table III.

The complex formation constants found in the present work are seen to be in reasonable agreement with those found by other methods. The reported values represent the constants for the addition of chloride ions to the neutral $AgCl$ complex, to form the anionic complexes $AgCl_{i+1}^-$. It is seen that in the solution phase the predominant complex is $AgCl_3^{2-}$ as was assumed for the resin phase. The formation of $AgCl_4^{3-}$ takes place only at high values of chloride ion activity (all the reported values of $\log \beta'_3$, β'^{-1}_{-2} are negative).

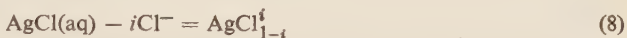
* No attempt was made to evaluate the activity coefficient functions γ'_i , since too little information is at present available concerning activity coefficients of the salts in hydrochloric acid, although approximations could be used, based on electrolytes of similar valence type. If γ'_i is known for the range of predominance of the i -th complex, it is possible to calculate the thermodynamic equilibrium constant β'_i from the parameter β_i^* .

TABLE III

Comparison of complex formation constants β'_i reported for the silver-chloride system

Author	Method	Medium	$\log \beta'_{-1}$	$\log \beta'_{-2}$	$\log \beta'_{-3}$	$\log \beta'_{-2}\beta'^{-1}_{-1}$	$\log \beta'_{-3}\beta'^{-1}_{-2}$
Forbes ⁸	soly.	varying				0.31 ^b	-0.41 ^b
Erber ⁹	soly.	varying				~ 1.0	~ -1.0
Jonte ¹⁰	soly.		1.96				
			1.67 ^b				
Berne ¹¹	soly.	0.2M NaClO ₄	1.88				
		5.0M NaClO ₄	2.32	3.20	2.22	0.88	-0.98
Leden ¹²	potent.	5.0M NaClO ₄					-1.0
Fomin ¹³	soly.		1.84				
Pinkus ¹⁴	soly.		1.82 ^b				
Jaques ¹⁵	soly.						-0.54 ^b
Kratohvil ¹⁶	soly.		1.88	2.11	1.71	0.23	-0.40
Present work	anion exch.	varying HCl	2.5	3.35	2.25	0.85	-1.1

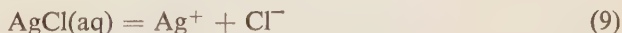
(a) The constants β'_i refer to the reaction:



the i value denoting the net charge of the species. The constant β'_i/β'_{i+1} is the equilibrium constant for forming the i -th complex from the $i+1$ complex.

(b) These values were calculated by Kratochvil, Tezak and Vouk¹⁶ from data of the stated authors.

It is seen in Figure 3 that the maximum in the curve for $\log D^0$ vs. $\log a$ occurs at or below* $\log a = -2.5$. This sets an upper limit of about -2.8 for $\log \beta'_{+1}$, the equilibrium constant for the reaction:



Thus we have the sequence for the $\log \beta'_i$ values for $i = +1, 0, -1, -2$, and -3 of $\leq -2.8, 0.0, 2.5, 3.35$, and 2.25 . The conventional (Bjerrum) stepwise formation constants $\log \beta_{(n)}^* \beta_{(n-1)}^{*-1}$ for forming the complex AgCl_n from AgCl_{n-1} are thus found to have for $n = 1, 2, 3$, and 4 the values $\geq 2.8, 2.5, 0.85$, and -1.1 .

ACKNOWLEDGMENT

The author wishes to thank the Scientific Director of the Israel Atomic Energy Commission for his help and his permission to publish this work and Professor Charles D. Coryell of the Massachusetts Institute of Technology for his help in the preparation of this paper.

* The rise in the curve for $\log D$ vs. $\log a$ in Figure 1 occurring below $\log a = -1.0$ is a consequence of the rise in the $\log \mu a$ curve (Figure 2) in the same region, which is multiplied by the factor $p = 2$ in correcting to the reference state by Eq. (2).

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THE THERMAL HYDROLYSIS OF METAL CHLORIDES.

I. CUPRIC CHLORIDE AND NICKEL CHLORIDE

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ABSTRACT

The thermal hydrolysis of anhydrous cupric (305–400°C) and nickel chloride (400–480°C) was investigated. In both cases hydrolysis was proved to occur at the interface with an adsorbed water layer. The products of hydrolysis were copper oxychloride (Cu_2OCl_2) and nickel oxide (NiO) respectively.

From the measured rate constants k , at various temperatures, the heat of the reaction by which copper oxychloride is formed, 13.3 kcal/g equiv. hydrogen chloride gas, and the activation energy of the hydrolytic reaction of nickel chloride, 18.6 kcal/mole, were obtained.

INTRODUCTION

The structure of metal chlorides ranges from fibrous open structures or laminar plates to closely packed ionic lattices. Since one would expect that along with these variations in structure there would be a corresponding variation in the mechanism of thermal hydrolysis, a comparative study of the thermal hydrolysis of a series of metal chlorides was carried out.

In the present article, results with cupric chloride and nickel chloride are reported. In cupric chloride dihydrate there are discrete planar groups of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, arranged in the *cis*-form¹. In the anhydrous salt all four sites of coordination are occupied by chlorine atoms, each pair of which bridges between two neighbouring copper atoms, whereby infinite chains are formed^{2,3}. The copper-chlorine distances for both compounds are the same, and largely covalent. The anhydrous nickel chloride, on the other hand, is ionic, and has a hexacoordinated layer structure of the CdCl_2 type^{3,4}.

EXPERIMENTAL

a) Materials

Cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, from May and Baker and J. T. Baker "Analysed" Reagent were employed. M&B crystals were larger than J. T. Baker crystals, and reacted somewhat more slowly than the latter. In this work only experiments with J. T. Baker samples are reported.

Anhydrous nickel chloride was prepared by dehydration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ "Baker Analysed" at 180–200°C in an atmosphere of hydrogen chloride⁵, and kept in a desiccator over phosphorus pentoxide.

* This article is part of a thesis to be submitted to the Senate of The Hebrew University of Jerusalem in partial fulfilment of the requirements for the Ph. D. degree.

Received August 28, 1958.

The mean of two analyses of this preparation gave:

	% Ni	% Cl	Total
Theoretical:	45.18	54.82	100
Found:	44.62	54.59	99.21

b) Apparatus

The reaction vessel was a Pyrex glass tube wrapped in heating coils and asbestos cords. This was connected at one end to the conductivity cell already described⁶ and to a wash bottle with a fritted glass bubbler at the other end. The wash bottle was placed in a thermostat at 26.5°C in order to impart to the constant flow of nitrogen gas a predetermined water vapour pressure. This aim was attained by placing in the wash bottle sulphuric acid solutions of known composition. The temperature of the oven was measured with a chromel–alumel thermocouple, and hand-regulated with the help of a "Sunvic-controller". The temperature read on the millivoltmeter remained constant within less than $\pm 2.5^\circ\text{C}$.

c) Procedure

The weighed samples were spread out in a porous porcelain boat 65 mm long, or in a platinum boat 15 mm long, so that they covered the bottom of the boat more or less evenly. Forty mg of the hydrated cupric chloride sufficed to cover the bottom of the porcelain boat, giving a layer equal to the thickness of the crystals (approx. 0.1 mm). With anhydrous nickel chloride, larger samples (~ 50 mg) were necessary for complete coverage of the same boat. The boat with the sample was introduced into the cooler part of the electric oven and the regulated gas current turned on. When the desired constant temperature had been attained, the boat was drawn, with the aid of a glass stopper winch and a nichrome wire, into the centre of the oven just underneath the soldered end of the thermocouple. The hydrogen chloride gas, driven by the gas current, was absorbed in a measured amount (125 ml) of distilled water in the conductivity cell. The cell was previously calibrated at 25°C, so that conductometric readings, taken at frequent intervals, could be directly converted into milli-equivalents or milligrams of hydrogen chloride. The room temperature was mostly a few degrees below 25°C, but the hot gases warmed up the solution in the conductivity cell to 27–28°C. All readings were therefore corrected for the observed deviation of the temperature of the solution from 25°C. When working with hydrated samples, soon after pulling the boat into the heated oven, some water droplets collected on the walls of the tube leading to the conductivity cell. In order to eliminate this unwanted condensation of water, this tube was heated by a separate coil to a temperature somewhat above 100°C. This precaution also eliminated the danger of any water vapour, liable to absorb hydrogen chloride gas, being condensed during an experiment in front of the conductivity cell.

Occasionally, at various stages of partial decomposition, the samples were quickly transferred to a desiccator packed with alumina or phosphorus pentoxide, and re-weighed after cooling. These samples were later analysed (a) for copper by a heterometric method⁷, (b) for nickel by the diacetyldioxime method, (c) for chloride, in acetic acid solution with dichlorofluorescein indicator or, in the case of nickel chloride, in a nitric acid solution by the Volhard method. The composition of the residues, as calculated from the conductivity measurements, could thus be checked.

In runs with cupric chloride dihydrate conducted at temperatures above 350°C, a greenish-brown substance sublimed and formed a thin deposit on the top of the cooler part of the oven. When the oven was allowed to cool, this sublimate turned white. The white powder dissolved in ammonium hydroxide solution, giving the characteristic blue colour of the cupric ion. The presence of some elementary chlorine was also ascertained by placing a piece of litmus paper in the current of the gases evolved: the litmus was completely bleached within a couple of hours. Neither of these effects amounted to more than 1–2% of the sample in all experiments below 375°C.

In the case of nickel chloride, sublimation was observed at all temperatures⁸. The amount of sublimate increased with the time of the reaction, as has been confirmed by analysis.

Some additional information on the decomposition product of cupric chloride was obtained from X-ray diffraction diagrams, for which we are indebted to Prof. E. Alexander, Dr. B. Fraenkel and Mr. A. Mustaky, all of the Department of Physics of The Hebrew University.

RESULTS

1. Cupric chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$)

The general appearance of the conductivity vs. time curves obtained is of the *S* type, as illustrated in Figure 1. The time of induction is about ten minutes. Following this, the increase of conductivity is linear up to close to 50% of the chlorine content of the sample, when the reaction comes almost to a standstill (with the exception of the run at 400°C). The slopes of the linear part of the curves were designated by *k*, and a number of factors, found to affect the rate of hydrolysis, were studied and compared by means of this constant.

(a) Spread and weight of the samples

In Table I are compared the slopes *k* of a few runs at 350°C, in which the spread of the samples ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and their weights were varied, other conditions being the same.

It can be seen that the *k* values are quite independent of the original weight of the samples (further examples are given in Table II), but vary considerably according to whether the sample is spread out or heaped. Consequently very small samples yield a correspondingly low constant *k*, whilst large samples tend to give high values. In

all further results reported here the samples were spread out to the full length of the boat (65 mm).

TABLE I
Slope 10k, at 350°C, varying spread and weight of sample

Sample wt. mg	Spread mm	10k	Sample wt. mg	Spread mm	10k
40.8	65	2.76	40.6	~30	1.74
150.8	65	2.62	150.6	~30	1.73
9.9	65	1.37			
301.2	65	3.11			

(b) *Rate of flow of nitrogen*

The 10k values of three series of runs, with ~40 mg samples, at 320°, 350° and 380°, in which the rate of flow had been widely varied, are plotted in Figure 2. During a run the flow metre showed fluctuations to the extent of $\pm 5\%$. With due consideration to irregularities arising out of this, it is evident from the figure that the slopes k are proportional to the rate of flow up to 34 ml/min in the series at 320° and to higher rates at more elevated temperatures. This linear relation does not hold at higher rates of flow. The series at 350° is also recorded in Table II, with some additional values of samples of varying weights (mostly 150 mg, marked with an asterisk).

TABLE II
Effect of rate of flow of nitrogen on the slope k at 350°

Flow (ml/min)	13.6	22.7	34.0	45.3	68.0	136
10k	1.23	1.80	2.76	2.62*	3.33	3.73
	1.34	1.92	2.52	2.69*	2.67	4.23
	1.38		2.53			4.33
Mean	1.32	1.86	2.62	3.00	4.10	5.55
Max. dev.	-7%	$\pm 3\%$	$\pm 4\%$	$\pm 11\%$	-9%	—

(c) *Partial pressure of water vapour in flow-gas*

Table III records the results of a series of runs at 365°C, flow rate 34 ml/min, in which the water vapour pressure in the flow-gas was varied. Evidently the k values are not affected by the water vapour pressure unless this is reduced below 0.1 mm Hg pressure.

TABLE III
Effect of variations in water vapour pressure on slope k

W. v. press. in mm Hg	0.1	0.25	0.4	0.5	2.75	26.0	
10 k	2.70	3.31	3.30	3.21	3.3	3.28	Mean: 3.24
		3.02					

(d) Induction Period

Increase of temperature or increase of rate of flow, as well as previous drying, reduce the period of induction.

(e) Total hydrolysis

The completion of the reaction, after 50% hydrolysis, is very slow and irregular. Following a stretch of about 90 min of slow hydrolysis, a somewhat faster evolution of hydrogen chloride is again observed. Also, the slope of the curve is steeper when the hydrolysis is continued next day, after having been interrupted for one night.

(f) Temperature coefficient

The $\log k$ values of the series of runs recorded in Figure 1 (with a few relative points added from Figure 2, +) were plotted, in Figure 3, versus the inverse absolute temperature. The points lie on a straight line, from the slope of which the heat content of the reaction, 13.3 Kcal/g equiv., was calculated (see Discussion).

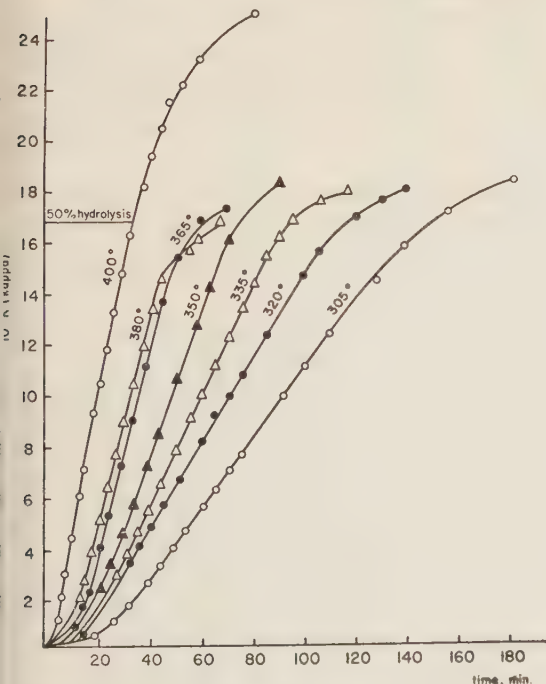


Figure 1

Conductometric measurements of the hydrolysis of cupric chloride at the temperatures indicated. Wt. of samples ~ 40 mg, flow rate (inert gas saturated with water vapour at room temperature) 34 ml/min

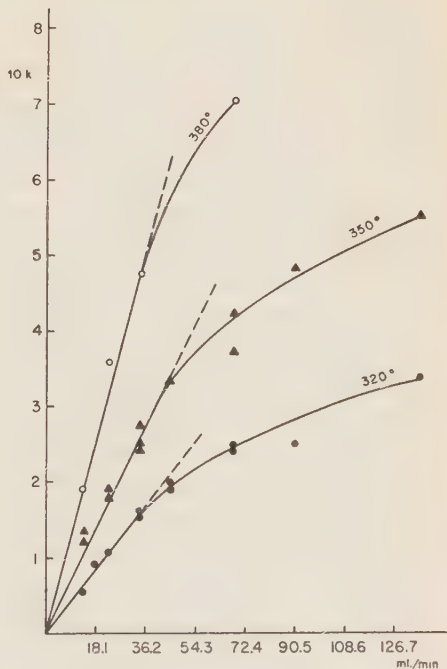


Figure 2

Influence of rate of flow of inert gas on the slope k at 320°, 350° and 380°C. CuCl_2

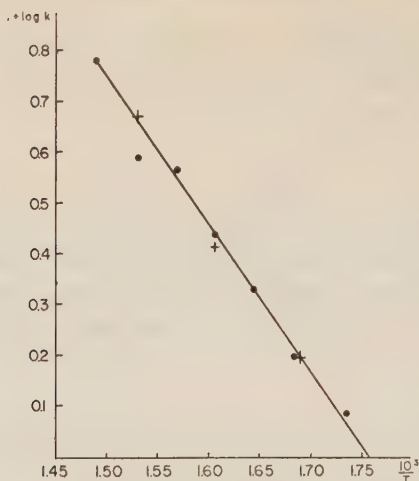


Figure 3

$\log k$ vs. $10^3/T$. CuCl_2 . Rate of flow of inert gas 34 ml/min; + indicates values taken from Figure 2

Analyses of partly hydrolysed samples

Most of the analyses were carried out on samples which initially weighed about 150 mg. The heterometric titrations of copper of the partially hydrolysed samples, as well as of the original cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, mostly yielded results too high by about 1.6%. The determination of copper by electrolysis, for larger samples of the dihydrate, gave theoretical values.

The chlorine content and the weight of several residues after partial hydrolysis are recorded in Table IV, and compared with the respective value calculated from the conductivity measurements. The amount of hydrolysis as evaluated from conductivity measurements is given in the Table under “% of hydrolysis”.

For chlorine, the agreement between calculated and titration values is satisfactory, considering that comparatively small samples were available for titration and that conductivity readings may be in error by 1–2%. Titrations often yielded somewhat higher results, with the exception of the samples hydrolysed at 375–400°C, in which case low results were obtained due certainly to the sublimation of some copper chloride, amounting to 5–6% of the original weight of the samples. The heterometric determinations of copper (not recorded in Table IV) confirmed this conclusion.

Calculations of the weight of the residues were made on the assumption that undecomposed chloride is present in its anhydrous form (CuCl_2) and that cupric oxide, or an oxychloride, is the ultimate product of the hydrolysis. The latter assumption is justified, because the hydroxylchloride, CuOHCl , prepared at 270°C, had a yellowish-green colour⁹, whilst our partly decomposed samples were dark brown to black. (See also the paragraph below on the interpretation of the X-ray diffraction diagrams). Also the agreement between the calculated and the actual weight of the residues is quite satisfactory for runs made at temperatures where sublimation is negligible.

It may therefore be concluded that: a) the cupric chloride is dehydrated at the very beginning of the hydrolysis, b) the conductivity measurements give a continuous and fairly accurate measure of the amount of hydrolysis, c) the product of hydrolysis is an oxide or an oxychloride, d) the amount of cupric chloride that sublimes is not more than 1–2% of the original weight of the sample at any temperature below 375°C.

TABLE IV
Analyses of partly hydrolysed samples

Wt. of sample (mg)	Temp. °C	% of hydrolysis	Wt. of residue (mg)		Cl ⁻ in residue (mg)	
			Calc.	Weighed	Calc.	Titrd.
151.7	325	31.6	104.25	104.5	43.2	—
149.6	337.5	52.1	92.9	86.7	29.9	30.6
150.0	337.5	28.1	104.75	102.2	44.9	46.3
149.8	337.5	29.5	103.9	100.8	44.0	45.7
42.9	350	58.6	25.6	22.4	—	—
78.6	350	45.3	50.5	47.6	—	—
151.0	350	40.6	99.4	104.2(?)	37.4	38.2
152.5	350	16.4	112.2	112.0	53.1	—
150.8	350	29.9	104.4	104.2	44.0	44.5
299.5	350	26.3	211.0	205.0	91.8	89.4
301.2	350	23.9	214.5	215.1	95.5	—
149.9	365	14.2	—	—	53.6	53.4
149.9	365	30.9	103.3	102.2	43.2	44.4
151.7	375	36.1	102.0	97.0	40.4	40.6
152.5	375	38.1	101.5	92.9	39.2	36.1
151.0	400	42.1	98.65	91.7	36.4	32.4
255.8	400	36.8	171.3	156.2	67.2	54.5

X-ray diffraction diagrams

A few X-ray powder diffraction diagrams of cupric chloride and of its partly decomposed products were taken. The line diagrams obtained for 1) an original sample of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 2) a sample kept in the oven up to the end of the induction period, 3) a sample in which hydrolysis was continued until 97% of the available hydrogen chloride was carried over to the conductivity cell, corresponded in the position of the lines, as well as in their intensities, to those recorded in the "X-ray diffraction card" of the American Society for Testing Materials for: 1) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 2) CuCl_2 anhyd., 3) CuO .

The diffraction diagram of a sample (4), for which hydrolysis was carried just to 50%, was distinct and different from any line diagram recorded in the literature, including Feitknecht's diagrams⁹ for the various forms of the copper hydroxy-chloride $\text{Cu}_2(\text{OH})_3\text{Cl}$ examined by him. Sample 5 which was heated for another 90 minutes (v.i.) after 50% hydrolysis, gave an identical line diagram to sample 4.

In Table V are recorded, for samples 3 and 4, the approximate relative intensities (*I*) of the measured lines and the distances (*d*) calculated from their positions, together with the corresponding values recorded for CuO in the catalogue.

TABLE V
Diffraction lines of samples 3 and 4

CuO Sample 3		Catalogue		Cu ₂ OCl ₂ Sample 4	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
				4	5.22
				10	4.88
				1	3.33
				5	2.94
1	2.74	12	2.75	5	2.77
10	2.51	100	2.52	9	2.49
				1	2.41
10	2.30	96	2.32	3	2.31
				5	2.16
				5	1.92
6	1.85	25	1.86	4	1.83
3	1.70	8	1.71	5	1.70
4	1.58	14	1.58	5	1.61
5	1.50	20	1.50	7	1.47
6	1.41	15	1.41	4	1.41
6	1.37	19	1.37	2	1.38
2	1.30	7	1.30	3	1.34
3	1.26	7	1.26	1	1.26
1	1.19	2	1.20	3	1.20
2	1.16	3	1.16	1	1.17
3	1.10	6	1.09		

It may be seen that there are some lines in the diffraction diagram of our sample 4 that vaguely correspond to those of sample 3, namely CuO. The relative intensities of these lines and the presence of some additional lines indicate, however, that sample 4 is a distinct compound of the general composition Cu₂OCl₂, containing 50% of the original amount of chlorine, as proved by analysis and conductivity measurements. The latter compound has been previously obtained under similar conditions (or by exchange with oxygen) by Jellinek and Rudat¹⁰ and by Korvezee¹⁰, who found that its heat of formation is equal to 91.5 kcal/mole. The X-ray diagrams thus fully confirm all conclusions arrived at on the evidence of the analytical results.

2. Anhydrous nickel chloride

The first experiments made with nickel chloride hexahydrate showed an initial fast increase in conductivity followed by a less steep linear plot (see Figure 4, broken line). The extent of the fast reaction was not controllable, and for this reason all further experiments recorded in the present article were made with anhydrous samples, which gave typical S curves when conductivity was plotted versus time. The slope of the middle part of these curves was constant (*k*) and extended to over 80% of the reaction. The influence of the various factors studied on the rate of hydrolysis is presented in Tables VI-VII and Figures 4-6.

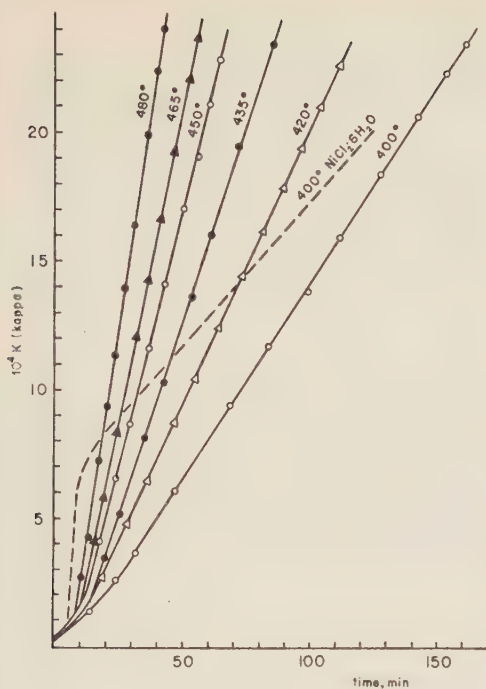


Figure 4

Conductometric measurements of the rate of hydrolysis of anhydrous nickel chloride at the temps. indicated. Wt. of samples ~ 50 mg, flow rate (inert gas satd. with water vapour at 26.5°C) 34 ml/min. Broken line shows experiment with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

Figure 5
Influence of water vapour pressure in flow gas on rate of hydrolysis of NiCl_2 .
pcn = porcelain boat;
Pt = platinum boat

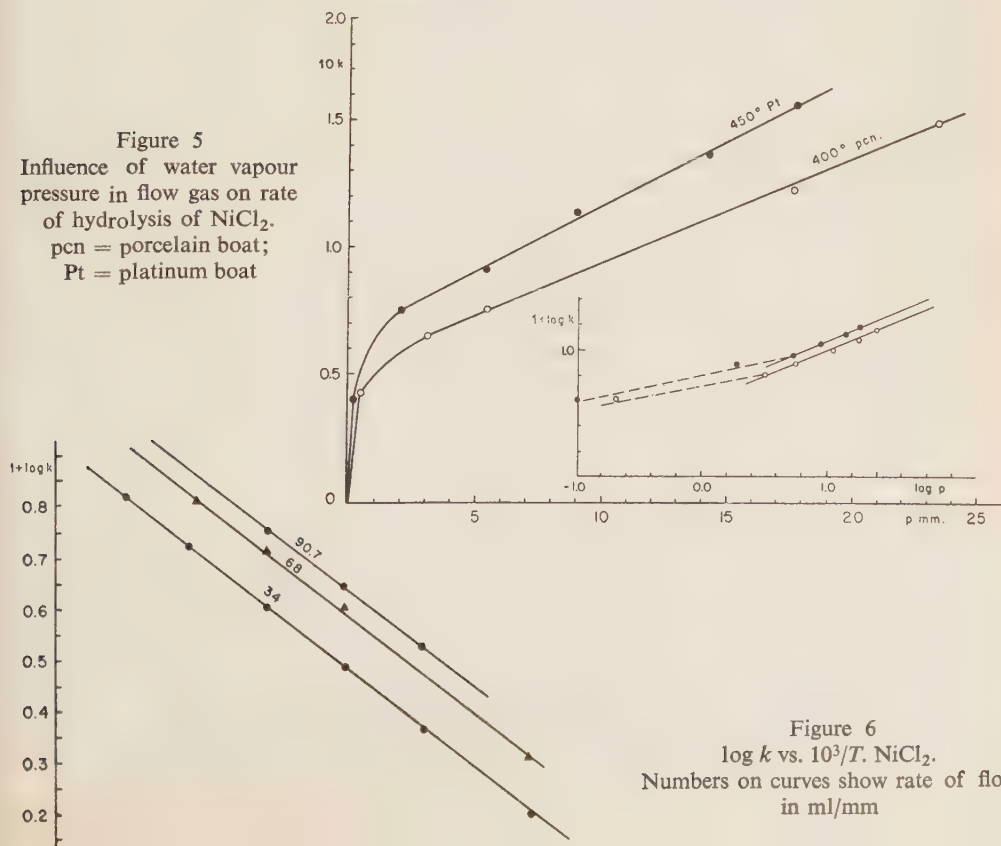


Figure 6
 $\log k$ vs. $10^3/T$. NiCl_2 .
Numbers on curves show rate of flow in ml/mm

A sevenfold variation of the *weight of the samples* did not affect the constants k (Table VI), in harmony with the apparent zero order of the hydrolysis. On the other hand, the *exposed surface* of the samples had a profound effect; the average of many experiments (under various conditions) gave for the porcelain and the much shorter and narrower platinum boats the ratio $k_{pcl}/k_{pt} = 2.4 \pm 0.1$ (see Tables VI-VII), where the k 's represent the respective constants.

The influence of the *rate of flow of nitrogen* is appreciable but much lower than that observed with cupric chloride. The equation $k = k_T \sqrt[3]{F}$ seems to be a good approximation for most values given in Table VII. (k_T = a constant for each temperature and F = rate of flow.)

The influence of *water vapour pressure* in the flow-gas may be seen in Figure 5. Two series of runs are shown, one in a porcelain boat at 400°C, and the other in a platinum boat at 450°C. In both cases, low vapour pressures cause a large increase in the constants k , and from a vapour pressure of about 1 mm Hg upwards the increase in k is linear, the two curves running nearly parallel. The slope of the plots $\log k$ vs. $\log p$ is 0.415 (see inset in Figure 5).

TABLE VI

The effect of weight and exposed surface of the samples on the slope k . Rate of gas flow: 34 ml/min, water vapour pressure 26 mm Hg

Temp. (°C)	400°			450°		
Weight (mg)	55.8	67.5	124.5	21.4	54.7	150.2
	1.50	1.37	1.46	4.0	4.0	4.2
10k	1.18 ^a			1.6 ^b		

a = porcelain boat, sample covered 1/3 of boat length

b = Pt boat

TABLE VII

The influence of the rate of flow of nitrogen on the slope 10k, at various temperatures; porcelain boat, ~50 mg samples, w.v. press. 26 mm Hg

Temp. °C	Rate of flow, ml/min			10k _T
	34.0	68.0	90.7	
400	1.50	2.00	—	0.47
420	2.16	—	3.31	0.70
435	3.05	4.00	4.41	0.97
450	4.00	5.24	5.61	1.26
465	5.15	2.18 ^b	6.33	1.57
480	6.75	2.78 ^b	—	2.08

b = Pt boat

Temperature coefficients

The influence of a rise of temperature (in the range 400–480°C) on the rate of hydrolysis may be seen from Figure 4. The $\log k$ values of three series of runs with

three different rates of flow of nitrogen were plotted against the inverse absolute temperature in Figure 6. The points lie on three parallel straight lines, from the slopes of which the energy value (assumed to be the activation energy of hydrolysis) of 18.6 kcal/equiv. is obtained.

In Table VIII *analytical results* for some partly decomposed samples are given. The residues were difficult to dissolve, obviously because of the insolubility of anhydrous nickel chloride¹¹. In order to obtain complete solution they were treated with nitric acid (1:1) at a low heat. Hence the chloride determinations are considered unreliable and, of the few titrations made, only two typical results are recorded in Table VIII.

The weight of the residues was always lower than calculated from conductivity data, indicating that some of the nickel chloride is lost by sublimation.

This sublimate collected on the walls of the cooler part of the oven and was identified as a compound of nickel. There is good correspondence between this loss of weight and the amount of nickel missing, as determined by analysis. Evidently sublimation is a side reaction (compare also time of a run and relative loss of weight in Table VIII) and does not invalidate the use of the constants k , which are independent of the bulk of sample.

TABLE VIII
Weight of partly hydrolysed samples and their analysis

Temp. °C	Wt. of sample (mg)	% of hydrol.	Time (mins)	Wt. of residue Calc. (mg)	Wt. of residue Weighed (mg)	Ni in residue Calc. (mg)	Ni in residue Weighed (mg)	Cl in residue Calc. (mg)	Cl in residue Detd. (mg)
400	53.7	32.1	142	45.5	43.6	23.9	22.0	19.6	17.7
	58.0	39.6	118	47.3	45.5	25.7	24.2	18.8	15.6
435	54.4	34.8	100	46.4	43.1	24.6	23.3	—	—
	59.6	35.3	73	50.7	48.8	—	—	—	—
	53.8	41.9	76	44.2	40.0	24.4	23.2	—	—
450	58.8	6.92	132	58.1	57.0				
	50.0	32.0	147	43.2	40.8				
	61.5	42.8	79	50.4	47.5				
	50.7	43.8	127	41.3	38.5				
	50.5	65.1	97	36.6	34.1				
	51.1	81.4	91	32.8	23.3				
480	53.1	59.8	61	39.5	34.4				
	50.3	87.3	106	31.0	24.8	22.3	18.7		

DISCUSSION

The analyses of partly decomposed samples, some of which were recorded in Tables IV and VIII, prove that the conductometric measurements show the actual state of hydrolysis of the sample at any moment during a run. With both anhydrous salts studied, namely, cupric and nickel chloride, S curves typical for reactions solid I \rightarrow solid II + gas were obtained. The main middle part of these curves was linear. Another common feature of the two reactions was their independence of the

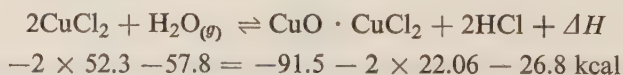
weight of the samples. On the other hand, the spread of the samples, i.e. the area of the exposed surface, had a more decisive effect on the rate of hydrolysis. Hence any explanation of the mechanism of these reactions must involve the surface area of the samples.

The possibility of a gaseous reaction close to the surface of the sample (so that the main part of the solid product is left in the boat) is very unlikely for many reasons. The most conclusive of these is the fact that, under conditions unfavourable for hydrolysis (e.g. at very low water vapour pressure), an increased loss due to sublimation has never been observed (see, for example, Table VIII, 450°C, 132 min, and compare with other experiments at the same temperature).

An interface reaction between the solid and an adsorbed water layer leads, on the other hand, to a consistent interpretation of the results. Judging by the influence of water vapour pressure on the constants k , the adsorbed water layer is saturated at a very low pressure in the case of cupric chloride, whilst in the case of nickel chloride a curve resembling a Freundlich isotherm is obtained. The behaviour of the two salts differs also in many other respects, hence they will be dealt with separately in the following.

The constants k for cupric chloride increase linearly when the flow rate of the inert gas is increased. At high flow rates this linearity fails to some extent (Figure 2). As the water vapour pressure has no influence, this deviation must be linked to the rate of removal of the hydrogen chloride from the site of the reaction, whilst the linear part of the curve points to a constant pressure of hydrogen chloride in the adsorbed layer, corresponding to the constant water vapour pressure. That is, at slow flow rates an equilibrium is established in the adsorbed layer, the removal of the hydrogen chloride being much slower than its rate of formation.

One may further assume, as a first approximation, a negligible temperature effect on the adsorbed water layer and on the rate of diffusion of hydrogen chloride from this layer, compared with the temperature effect on the equilibrium pressure of the hydrogen chloride in the adsorbed layer. Hence the measured constants k at various temperatures are proportional to the equilibrium pressure of the hydrogen chloride in the adsorbed layer, at least at slow rates of flow, and the slope of the curve obtained on plotting the $\log k$ values versus temperature (Figure 3) indicated the heat of reaction whereby the cupric oxychloride is formed. This conclusion is confirmed by calculation from data available in the literature¹².



ΔH is seen to be twice the value 13.3 kcal/g equiv. obtained in this work.

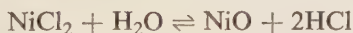
The heat of formation of CuCl_2 from its elements is given by Shchukarev and Oranskaya⁸ as -41.2 kcal., but this involves a corresponding change in the heat of formation of the cupric oxychloride¹⁰ $\text{CuCl}_2 \cdot \text{CuO}$, leaving ΔH the same as above.

The formation, stability and entity of the cupric oxychloride Cu_2OCl_2 up to 380°C has been amply proved by the conductivity-time curves, analyses and X-ray diffraction diagrams.

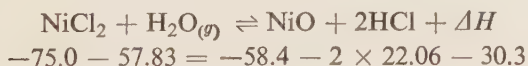
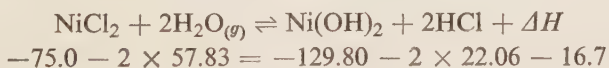
In accordance with the absence of any effect of water vapour pressure (Table III), the original samples of the dihydrate were completely dehydrated during the induction period before any appreciable hydrolysis occurred. This fact is clearly due to the comparatively slow attack of water vapour on the covalent copper-chlorine bond and to the close packing of the fibrous anhydrous cupric chloride in the crystals impermeable to water vapour.

In the case of anhydrous nickel chloride, characterised by ionic bonds and a layer structure, matters are quite different; the hydrolysis of the hydrated samples proceeds at a much faster rate than that of the anhydrous preparations. Also, an increase of water vapour pressure increases the rate of hydrolysis to some extent, indicating a limited diffusion of the water molecules between the crystal layers.

The rate of flow of inert gas has a small but appreciable effect on the constants k , and can be attributed only to the faster removal of the hydrogen chloride, preventing a back reaction. This effect, being the same under various conditions such as temperature and exposed surface (Table VII), shows that the determining factor of all the chemical and physical reactions involved is that of the hydrolysis. Therefore, the slopes of the curves in Figure 6 represent the activation energy, 18.6 kcal/mole, of the hydrolytic reaction:



which is larger than the heat of formation of $\frac{1}{2}\text{Ni}(\text{OH})_2$, and much smaller than the heat of formation of NiO^{12} in the following reactions:



To sum up, the hydrolysis of both anhydrous chlorides is an interface reaction with an adsorbed water layer. The observed time of induction may be due to the building up of this layer or to nucleation, or both. In the case of nickel chloride there may also occur a limited diffusion of water molecules between the lattice layers.

In experiments with the hydrates, the hydrolytic reaction proper proceeds at a rate comparable to the rate of dehydration, in the case of nickel chloride, but at a much slower rate in the case of cupric chloride. This difference is attributed to the difference in the nature of the chemical bonds in the two chlorides. In harmony with this conclusion, the hydrogen chloride produced in the hydrolysis is much more strongly held in the adsorption layer by the cupric chloride, and a much stronger

current of flow-gas is needed to remove it, than in the case of nickel chloride. On this fact depends the interpretation of the meaning of the constants k ; in the case of cupric chloride k reflects the equilibrium pressure of the hydrogen chloride in the adsorbed layer, whilst in the case of nickel chloride it reflects the rate of the hydrolytic reaction proper. The energy values derived from the temperature coefficients of the two respective reactions appear to confirm this conclusion.

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LETTER TO THE EDITOR

The stereochemical mechanism of starch hydrolysis by α -amylase. M. HALPERN AND J. LEIBOWITZ,
Department of Biological Chemistry, The Hebrew University of Jerusalem.

In a former communication¹ we established the fact that β -amylase splits intersaccharidic linkages in the starch molecule at the point between the carbon C_1 and the oxygen bridge. This creates at the anomeric carbon atom the conditions for a Walden inversion in accordance with the experimental production of β -maltose only from starch by β -amylase. The method of our investigation was the use of heavy water (H_2O^{18}) as a tracer compound and the subsequent determination of the position of the O^{18} at C_1 in the sugar molecule. Continuing the investigation with α -amylase which produces from starch some glucose besides the maltose, the same results were obtained, i. e. that the whole O^{18} was bound to the anomeric carbon atoms. It follows that α -amylase also splits the saccharidic bond at the anomeric carbon atom. As, nevertheless, the hydrolysis in this case is not accompanied by a Walden inversion, it must be concluded that the mechanism is one of double displacement. These observations prove that although Walden inversion cannot take place without the bond being cleaved at the anomeric carbon atom, such an inversion is not always a result of that cleavage. What affects the inversion is the exact orientation of the active and complementary groups of the enzyme and substrate.

Following our first communication¹ on the hydrolysis of starch with β -amylase, F. C. Mayer and J. Larner² in a recent note announced the results of a similar investigation of the cleavage points of α - and β -amylases in the glycogen molecule. With both amylases their results with glycogen are identical with our findings with starch. In view of the close structural resemblance of amylopectin and glycogen, the agreement between these results had to be expected.

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Received October 18, 1958.

NEWS AND VIEWS

PRELIMINARY NOTICE
of the
2nd INTERNATIONAL CONGRESS OF POLAROGRAPHY
Organised by the
POLAROGRAPHIC SOCIETY
TO BE HELD AT CAMBRIDGE, AUGUST 24-29, 1959

The 2nd International Congress of Polarography, to be held at the University of Cambridge, August 24-29, 1959, will consist of Scientific Sessions (original papers, reviews and discussions), an Exhibition of Commercial Equipment, Demonstrations of Laboratory Apparatus, visits to local industry and places of interest, and social functions.

Professor Heyrovsky, head of the Polarographic Research Institute of the Czechoslovakian Academy of Sciences and the President of the Polarographic Society, has agreed to give the opening address; the proceedings will be published in book form and will be dedicated to Professor Heyrovsky's 70th birthday.

A supporting programme for ladies is being arranged.

The scientific programme will be divided into the following Sections: —

1. Instrumentation.
2. Theory and Kinetics.
3. Analytical and Industrial Applications.
4. Fundamental Studies.
5. Biological and Medical Applications.
6. Miscellaneous.

There will also be four Plenary Lectures by world authorities and six Section Lectures.

Contributions will be welcome and details should be submitted to: —

G. F. Reynolds, M.Sc., F.R.I.C.,
Chemical Inspectorate, Ministry of Supply
C. 36. Royal Arsenal,
Woolwich, London, S.E. 18, England.

Notification of intention to submit a communication should be made as soon as possible and in no case later than March 31, 1959, by which date a summary not exceeding 200 words is also required.

Preprints of all papers will be issued and final manuscripts must therefore be received not later than May 31, 1959.

Requests for application forms and further details should be sent to: —

Mrs. B. Lamb, B.Sc., F.R.I.C.
Chemistry Laboratory
Evershed and Vignoles
Corner of Eveagh Avenue
North Circular Road
London, N.W. 10, England.

The keys to the lettering on the curves in these two figures was inadvertently omitted from the originally published form of the graphs. The correct forms, including the keys, are reproduced below.

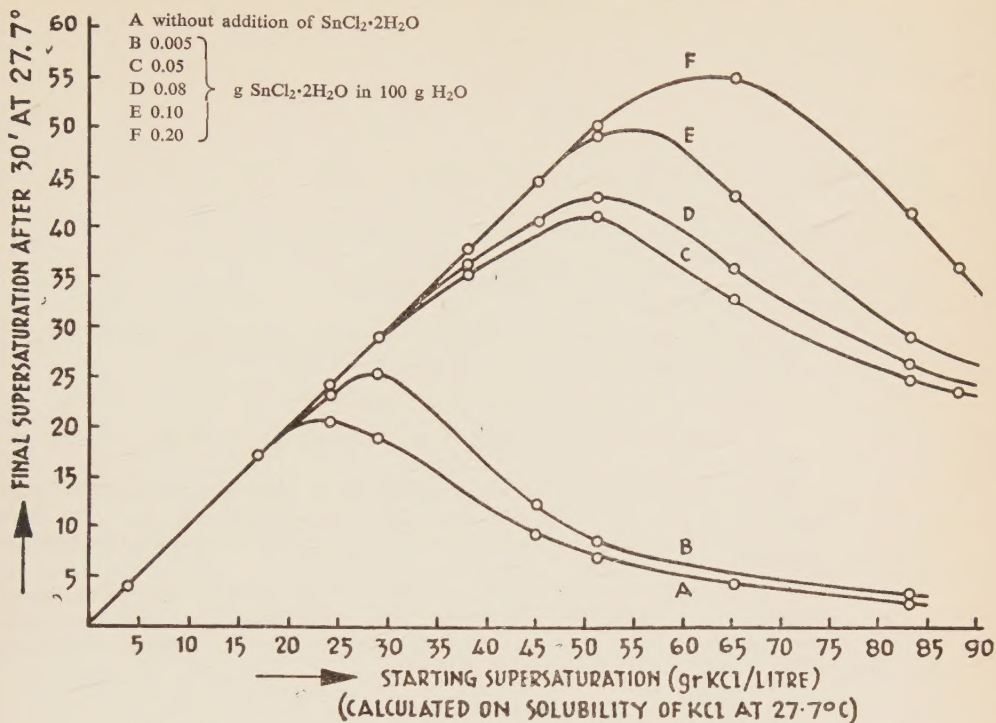


Figure 2. Stabilising effect of stannous chloride on supersaturation of KCl

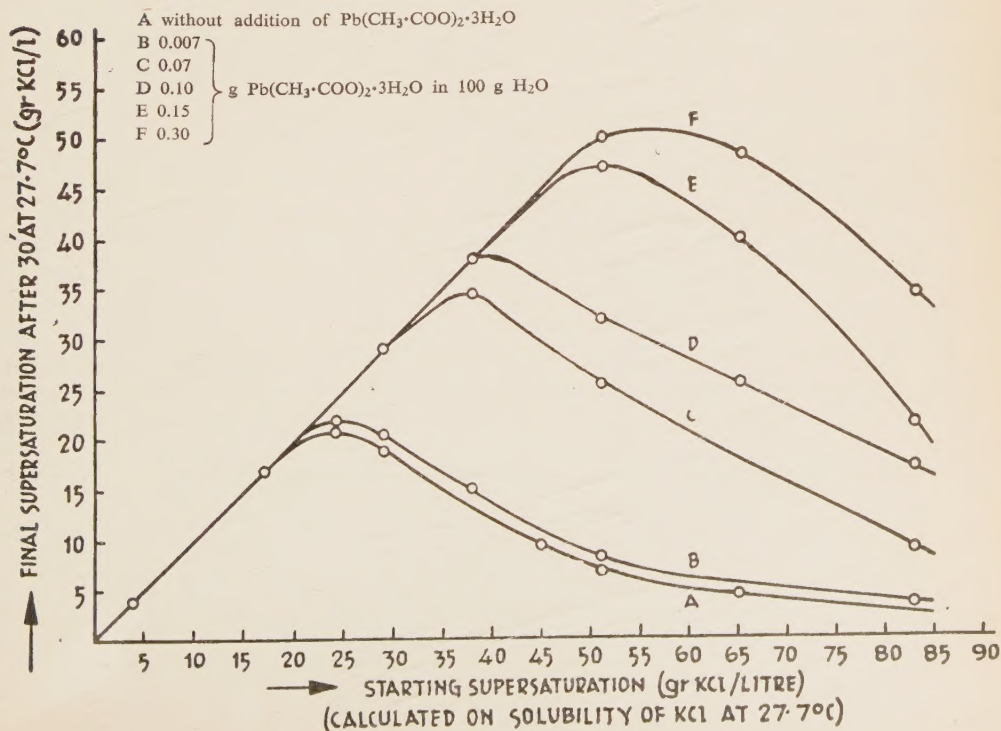


Figure 3. Stabilising effect of lead acetate on supersaturation of KCl

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Published by

THE WEIZMANN SCIENCE PRESS OF ISRAEL

Research Council of Israel, Ministry of Education and Culture

The Hebrew University of Jerusalem, Technion—Israel Institute of Technology

The Weizmann Institute of Science, Bialik Institute

Printed in Israel

Raphael Haim Hacohen Press, Ltd., Jerusalem

WSP/1000/2.59